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(54) Title: CONTROLLED FREE RADICAL EMULSION AND WATER-BASED POLYMERIZATIONS AND SEEDED METHODOLOGIES																		
(57) Abstract  Nitroxides having an alpha-carbon atom with a destabilizing moiety are effective control agents for emulsion and water-based polymerizations, including the formation of block copolymers from a wide range of monomers. The nitroxide radicals may be used as a free radical or as an adduct with a residue from the initiator. The emulsions have living characteristics, including the re-initiation of polymer chains. Also, a seeded process for emulsions, which includes the step-wise addition of monomer is disclosed, providing access to a wide range of initiator types.																		

**CONTROLLED FREE RADICAL EMULSION AND WATER-BASED  
POLYMERIZATIONS AND SEEDED METHODOLOGIES**

5        This application claims priority under 35 U.S.C. § 119 to the commonly owned, co-pending U.S. Provisional Application No. 60/123,498, filed March 9, 1999, which is incorporated herein by reference in its entirety. This application is also a continuation-in-part of each of U.S. Patent Applications No. 09/347,606, No. 09/347,607, No. 09/347,608 and No. 09/347,609, each of which was filed July 2, 1999, and each of which is incorporated herein  
10      by reference in its entirety.

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

15      This invention pertains to methods and compositions for controlled free radical polymerization in an emulsion or aqueous system using free radicals that provide control under a variety of conditions and with a wide variety of monomers. This invention also pertains to methods for seeding emulsion polymerizations. Furthermore, this invention also pertains to the polymers, copolymers and interpolymers that can be made with such a system.

**Background Discussion**

20      Controlled free radical polymerizations are generally known, which provide "living" type kinetics. These reactions may proceed by stable free radical or other mechanism. With the stable radical mechanism, it is generally believed that a stable free radical is used to reversibly cap the propagating polymer chain. There are several well-known nitroxide radicals (e.g., nitroxyls) that may be usefully employed in this methodology. See, e.g., U.S. Patents 4,581,429, 5,322,912 and 5,401,804, each of which is incorporated herein by  
25      reference. The nitroxide radicals disclosed in these references have  $\alpha$ -carbon atoms attached to the nitrogen that bear alkyl or aryl moieties (in addition to the oxygen). One of the most

The use of water as a dispersing medium or solvent for control free radical polymerization is commercially important for several reasons. First, water is the safest medium from an environmental viewpoint, facilitating the manufacture of consumer products (such as paints or glues). Also, water is one of the least expensive media, providing an 5 economical process. Moreover, the emulsion polymerization process is unique in that aqueous dispersions and emulsion that have direct utility in this for in various applications.

Also, seeded emulsion polymerizations are generally known in order to avoid or simplify the nucleation step. See, e.g., Poehlein *et al.*, "Characterization of Water-Soluble Oligomer in Acrylic Acid-Styrene Emulsion Copolymerization," *J. Appl. Polym. Sci.*, vol. 50, 10 pp. 2173-2183 (1993) or Ugelstad, *et al.*, "A kinetic Investigation of the Emulsion Polymerization of Vinyl Chloride," *J. Polymer Sci., Part C*, no. 27, pp. 49-68 (1969), both of which are incorporated herein by reference. Seeded emulsions have also been attempted with TEMPO and TEMPO-like free radicals. See German *et al.* (cited above). The problem with these attempts is that the systems did not provide particle size control or emulsion quality for 15 commercially important emulsions.

A need exists for a versatile, water-based controlled free radical polymerization process, which can use many types of initiators and can polymerize many types of monomers with a wide variety of process conditions.

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#### SUMMARY OF THE INVENTION

This invention provides a method of free radically polymerizing a wide variety of monomers using water-soluble systems or emulsions, and thus provides access to a wide variety of resultant polymers that may be made from such processes. The methods, emulsions and polymers of this invention provide living-type free radical polymerizations, 25 including the ability to re-initiate polymer chains and thus prepare unique polymers, including block copolymers. It is thus an object of this invention to provide a polymerization process that allows access to a wide variety of monomers that may be polymerized alone or together in emulsions or in an aqueous solution system. Moreover, the methods of this invention enable access to a full range of initiators, including fast and water-soluble initiators 30 as well as slow and organic-soluble initiators that might otherwise appear to be less favorable for aqueous-based living-type polymerizations.

invention is block copolymers having blocks with a weight average molecular weight of at least about 25,000.

Other aspects of this invention will be evident to those of skill in the art upon review of this specification, drawings and examples.

5

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B are graphs showing molecular weight and conversion as a function of increasing nitroxide radical concentration for the TEMPO-controlled heterogeneous polymerization of styrene;

10 FIGS. 2A and 2B are graphs showing molecular weight and conversion as a function of increasing concentration of an  $\alpha$ -hydrido nitroxide control agent for the heterogeneous polymerization of styrene.

15 FIGS. 3A-3E are graphs demonstrating the living kinetics achieved with this invention as well as control of molecular weight and conversion based concentration of an  $\alpha$ -hydrido nitroxide radical control agent.

FIG. 4 is a bar graph showing molecular weight as a function of the concentration of an  $\alpha$ -hydrido nitroxide radical control agent for both styrene polymers and styrene/butylacrylate copolymers.

20 FIG. 5 is a bar graph showing molecular weight as a function of the concentration of an  $\alpha$ -hydrido nitroxide control agent for both butylmethacrylate polymers and styrene/butylmethacrylate copolymers.

FIG. 6 is a bar graph showing molecular weight as a function of the ratio of monomer to initiator for both styrene polymers and styrene/butylacrylate copolymers.

25 FIG. 7 is a bar graph illustrating the reinitiation of a living free radical polymerization after the addition of *n*-butylacrylate according to the invention.

FIG. 8 is a bar graph illustrating the reinitiation of a living free radical polymerization after the addition of acrylic acid according to the invention.

FIG. 9 is a bar graph illustrating the relationship between the overall molecular weight of the random copolymer and the amount of acrylic acid described in the example.

methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), hexyl, vinyl, n-butyl, tert-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

“Substituted alkyl” refers to an alkyl as just described in which one or more hydrogen atom to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, and combinations thereof. Suitable substituted alkyls include, for example, benzyl, trifluoromethyl and the like.

The term “heteroalkyl” refers to an alkyl as described above in which one or more hydrogen atoms to any carbon of the alkyl is replaced by a heteroatom selected from the group consisting of N, O, P, B, S, Si, Se and Ge. The bond between the carbon atom and the heteroatom may be saturated or unsaturated. Thus, an alkyl substituted with a heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, or seleno is within the scope of the term heteroalkyl. Suitable heteroalkyls include cyano, benzoyl, 2-pyridyl, 2-furyl, Me<sub>3</sub>SiOCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C— and the like.

The term “cycloalkyl” is used herein to refer to a saturated or unsaturated cyclic non-aromatic hydrocarbon radical having a single ring or multiple condensed rings. Suitable cycloalkyl radicals include, for example, cyclopentyl, cyclohexyl, cyclooctenyl, bicyclooctyl, etc. In particular embodiments, cycloalkyls have between 3 and 200 carbon atoms, between 3 and 50 carbon atoms or between 3 and 20 carbon atoms.

“Substituted cycloalkyl” refers to cycloalkyl as just described including in which one or more hydrogen atom to any carbon of the cycloalkyl is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted cycloalkyl radicals include, for example, 4-dimethylaminocyclohexyl, 4,5-dibromocyclohept-4-enyl, and the like.

The term “heterocycloalkyl” is used herein to refer to a cycloalkyl radical as described, but in which one or more or all carbon atoms of the saturated or unsaturated cyclic radical are replaced by a heteroatom such as nitrogen, phosphorous, oxygen, sulfur, silicon, germanium, selenium, or boron. Suitable heterocycloalkyls include, for example, piperazinyl,

ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

- 5        "Substituted heteroaryl" refers to heteroaryl as just described including in which one or more hydrogen atoms to any atom of the heteroaryl moiety is replaced by another group such as a halogen, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, boryl, phosphino, amino, silyl, thio, seleno and combinations thereof. Suitable substituted heteroaryl radicals include, for example, 4-N,N-  
10 dimethylaminopyridine.

The term "alkoxy" is used herein to refer to the  $-OZ^1$  radical, where  $Z^1$  is selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, silyl groups and combinations thereof as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, benzyloxy,  
15 t-butoxy, etc. A related term is "aryloxy" where  $Z^1$  is selected from the group consisting of aryl, substituted aryl, heteroaryl, substituted heteroaryl, and combinations thereof. Examples of suitable aryloxy radicals include phenoxy, substituted phenoxy, 2-pyridinoxy, 8-quinalinoxy and the like.

As used herein the term "silyl" refers to the  $-SiZ^1Z^2Z^3$  radical, where each of  $Z^1$ ,  $Z^2$ ,  
20 and  $Z^3$  is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.

As used herein the term "boryl" refers to the  $-BZ^1Z^2$  group, where each of  $Z^1$  and  $Z^2$  is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, amino, silyl and combinations thereof.  
25

As used herein, the term "phosphino" refers to the group  $-PZ^1Z^2$ , where each of  $Z^1$  and  $Z^2$  is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, cycloalkyl, heterocycloalkyl, heterocyclic, aryl, heteroaryl, silyl, alkoxy, aryloxy, amino and combinations thereof.  
30

The term "amino" is used herein to refer to the group  $-NZ^1Z^2$ , where each of  $Z^1$  and

Alkoxyamine for 'Living' Free Radical Polymerizations," *J. Am. Chem. Soc.*, 1999, 121(16), pp. 3904-3920; all of which are incorporated herein by reference. These patents, patent applications and publications disclose a wide variety of nitroxide radical control agents, which in general can be characterized by the general formula  $\bullet\text{O}-\text{NR}_2$  wherein each R is independently selected from the group consisting of hydrocarbyl and substituted hydrocarbyl, and optionally the two R's may be joined together.

5

In some preferred embodiments of this invention, the free radical control agents may be characterized by the general formula:



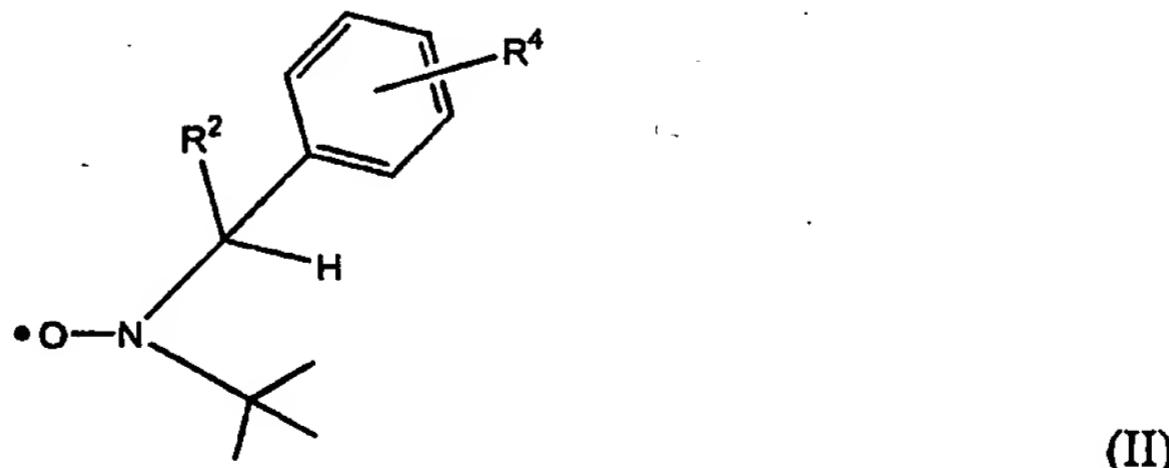
10 where each of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and optionally, R<sup>1</sup> and R<sup>2</sup> are joined together in a ring structure; and also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in  
15 a ring structure. X is a moiety that is capable of destabilizing the free radical, such as hydrogen. By "capable of destabilizing" it is meant that the X moiety allows the free radical to destabilize, decompose, be destroyed or otherwise removed from the reaction mechanism or be destabilized, decomposed, destroyed or removed from the reaction by the addition of a reagent. Generally, there is only destabilizing moiety on a carbon that is in the alpha ( $\alpha$ ) position. Thus, when X is hydrogen, the group chosen for R<sup>3</sup> should not include a hydrogen on the atom bonded to the nitrogen atom; such that R<sup>3</sup> is typically selected from the group  
20 consisting of tertiary alkyl, substituted tertiary alkyl, aryl, substituted aryl, tertiary cycloalkyl, substituted tertiary cycloalkyl, tertiary heteroalkyl, tertiary heterocycloalkyl, substituted tertiary heterocycloalkyl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy and silyl. For the  
25 embodiments of this invention where it is desirable to enhance the water-solubility or transport of the control agent, it is preferred that one of the R groups (R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup>) includes a water-solubilizing group, such as a sulfonate, sulfate, carboxylate, hydroxyl, amino,

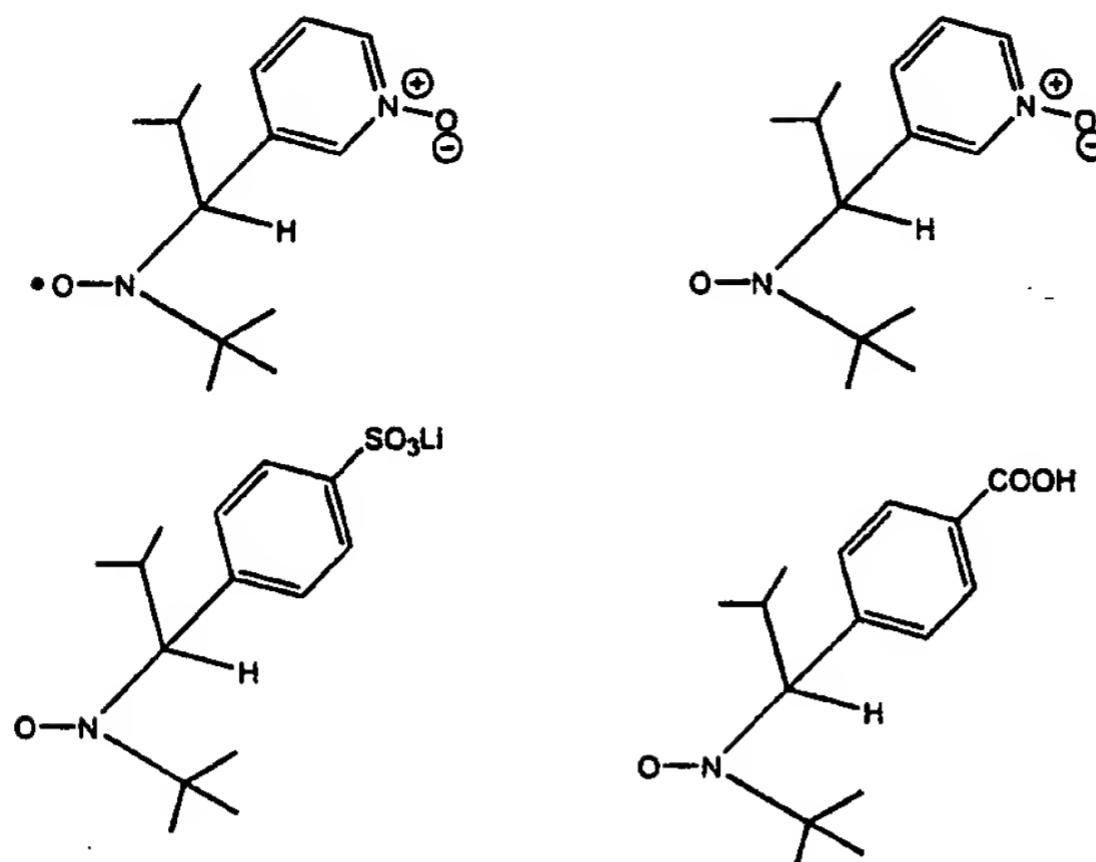
propagating chain ends depends on the exact polymerization conditions, monomers and nitroxide radicals, but typically is in the range of from about  $10^{-4}$  to  $10^{-8}$  moles per liter.

Another function of control agent structure in the heterogeneous aqueous polymerization mixtures of the invention is to influence the partitioning and concentration of control agent in the various phases of the mixture, such as the water phase, polymer phase, and or monomer phase, if present. Depending on the exact polymerization conditions, this partitioning can be important to the rates and living nature of polymerization at the intended locus of polymerization as well as other locations within the heterogeneous mixture.

In more specific embodiments, each R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from a group consisting of alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl and silyl. Specific examples of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, cyclooctyl, phenyl, benzyl, trimethylsilyl, those specific moieties listed in the above definitions and the like. In alternative embodiments, R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> may include a water-solubilizing group, such as SO<sub>3</sub>G, where G is Na, K and the like. In a preferred embodiment, R<sup>1</sup> is an aryl (such as phenyl), R<sup>2</sup> is an alkyl (such as isopropyl) and R<sup>3</sup> is either an alkyl or a heteroalkyl (such as *tert*-butyl or Me<sub>3</sub>SiOCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C—). In an alternative preferred embodiment, R<sup>1</sup> is an aryl (such as phenyl), R<sup>2</sup> is a cycloalkyl (such as cyclohexyl or cyclopentyl) or a tertiary alkyl (such as *tert*-butyl) and R<sup>3</sup> is either a tertiary alkyl or a heteroalkyl (such as *tert*-butyl or Me<sub>3</sub>SiOCH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>C—). In still another preferred embodiment, R<sup>1</sup> is a substituted alkyl (such as NC(CH<sub>3</sub>)<sub>2</sub>C—) and R<sup>2</sup>CNR<sup>3</sup> form a cyclic ring structure.

In other embodiments, the free radical control agents may be characterized by the general formula:





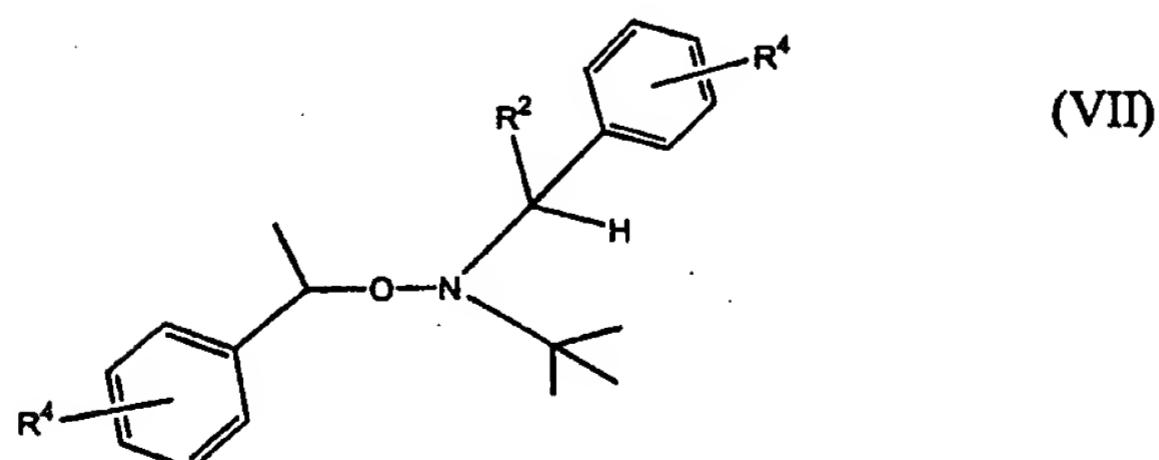
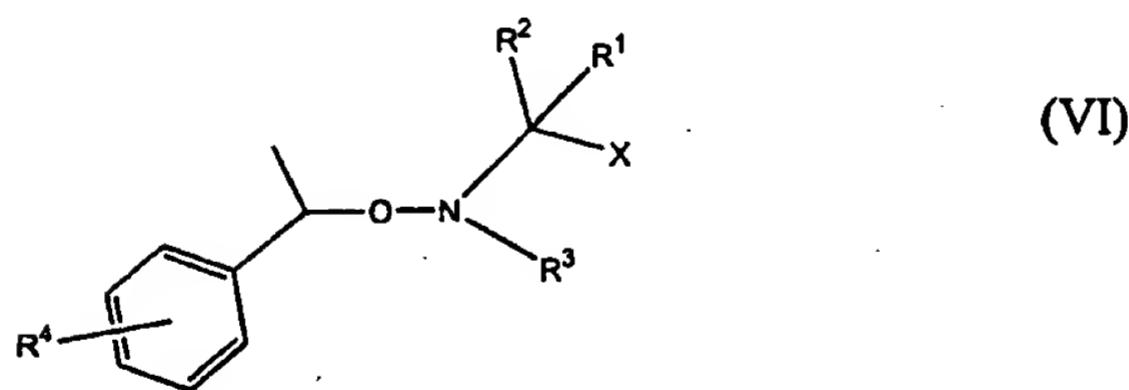
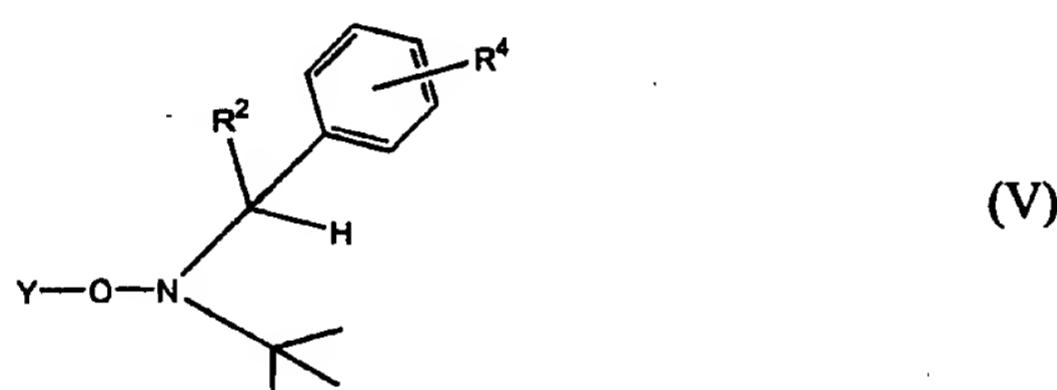
### Initiators

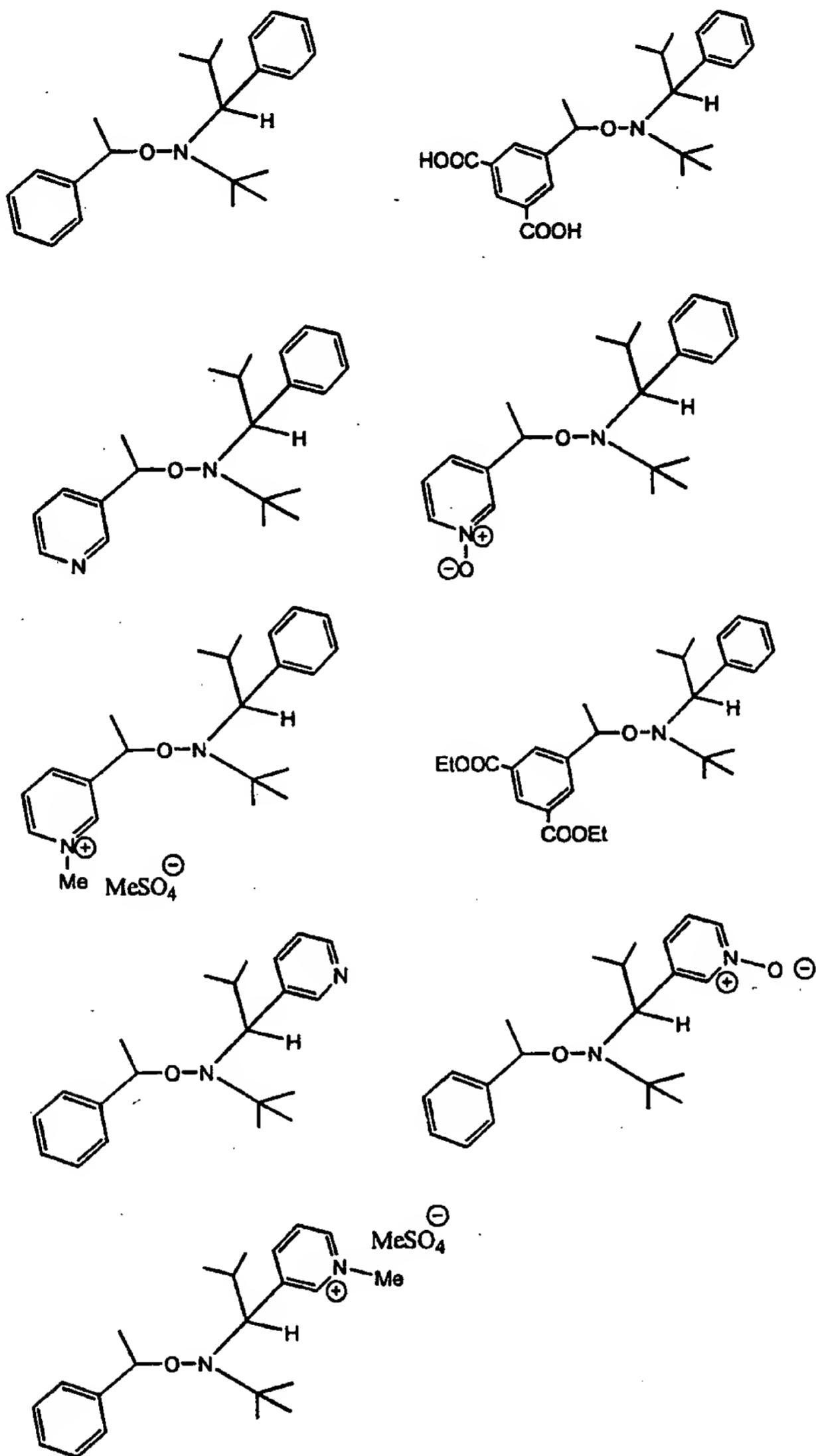
Initiators useful in this invention include both water-soluble initiators and solvent-soluble or monomer-soluble initiators. Generally, the initiator must be capable of producing a radical ( $Y\cdot$ ) that initiates radical polymerization of a monomer and may attach to an end of the polymer.

In general, suitable radical initiators (and from which the  $Y\cdot$  radical may be derived) can be selected from the group consisting of alkyl peroxides, substituted alkyl peroxides, aryl peroxides, substituted aryl peroxides, acyl peroxides, alkyl hydroperoxides, substituted alkyl hydroperoxides, aryl hydroperoxides, substituted aryl hydroperoxides, heteroalkyl peroxides, substituted heteroalkyl peroxides, heteroalkyl hydroperoxides, substituted heteroalkyl hydroperoxides, heteroaryl peroxides, substituted heteroaryl peroxides, heteroaryl hydroperoxides, substituted heteroaryl hydroperoxides, alkyl peresters, substituted alkyl peresters, aryl peresters, substituted aryl peresters, azo compounds and halide compounds. Specific initiators include cumene hydroperoxide (CHP), t-butyl hydroperoxide (TBHP), t-butyl perbenzoate (TBPB), sodium carbonateperoxide, benzoyl peroxide (BPO), lauroyl peroxide (LPO), methylethylketone peroxide 45%, potassium persulfate, ammonium persulfate, 2,2-azobis(2,4-dimethyl-valeronitrile) (VAZO®-65), 1,1-azobis(cyclohexanecarbonitrile) (VAZO®-40), 2,2-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride (VAZO®-044), 2,2-azobis(2-amidino-propane) dihydrochloride (VAZO®-

where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, Y and X have the above meanings and preferences. In this context, Y is a residue capable of initiating free radical polymerization upon homolytic cleavage of the Y—O bond, including, for example, alkyl, substituted alkyl, alkoxy, substituted alkoxy, heteroalkyl, substituted heteroalkyl, aryl, and substituted aryl residues. Use of such adducts  
 5 can eliminate concerns about the speed of initiation of polymer chains, effectively initiating all polymer chains at the same time upon addition of the adduct to the monomer under polymerization conditions. When the adduct is employed, the ratio of control agent to initiator can be adjusted by the addition of free radicals from any source, including, for example, additional free radical control agent (such as shown in connection with formula I,  
 10 above), additional free radical initiators or radicals derived from other reactions.

When the preferred formulas for the control agent and the initiating radicals are combined, the preferred adducts of this invention may be characterized by any of the following general formulas:





As discussed in various places throughout this specification, the hydrophilicity of the control agent, initiator and/or initiator-control agent adduct can be tuned to account for the desired water-transportability or water-dispersability or water-solubility. Generally, tuning the hydrophilicity comprises the use of one or more hydrophilic functional groups attached to

acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-*tert*-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-*tert*-butylacrylamide, N-n-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylaminostyrene (all isomers),  $\alpha$ -methylvinyl benzoic acid (all isomers), diethylamino  $\alpha$ -methylstyrene (all isomers), *p*-vinylbenzene sulfonic acid, *p*-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, butadiene, isoprene, chloroprene, ethylene, vinyl acetate, 2-(2-oxo-1-imidazolidinyl)ethyl 2-methyl-2-propenoate, 1-[2-[[2-hydroxy-3-(2-propyl)propyl]amino]ethyl]-2-imidazolidinone, *W*-vinyl pyrrolidone, N-vinyl imidazole, crotonic acid, vinyl sulfonic acid, and combinations thereof.

Depending on the embodiment of the invention being practiced, these monomers may be referred to as the first polymerizable monomer, the second polymerizable monomer, at least one monomer, etc.

include, for example, ethoxylated mono-, di- and trialkylphenols (degree of ethoxylation: 3 to 100, alkyl radical: C<sub>4</sub> to C<sub>12</sub>), ethoxylated fatty alcohols (degree of ethoxylation: 3 to 100, preferably 6 to 50, alkyl radical: C<sub>6</sub> to C<sub>20</sub>) and alkali metal and ammonium salts of alkylsulfates (alkyl radical: C<sub>8</sub> to C<sub>18</sub>), of sulfuric half-esters of ethoxylated alkanols (degree of ethoxylation: 1 to 70, in particular 2 to 10, alkyl radical: C<sub>10</sub> to C<sub>18</sub>) and of ethoxylated alkylphenols (degree of ethoxylation: 3 to 100, preferably 6 to 50, alkyl radical: C<sub>4</sub> to C<sub>18</sub>) and alkali metal and ammonium salts of alkanesulfonic acids (alkyl radical: C<sub>10</sub> to C<sub>18</sub>) and of alkylarylsulfonic acids (alkyl radical: C<sub>9</sub> to C<sub>18</sub>). Further suitable surfactants, such as sulfosuccinates, are described in Houben-Weyl, Methoden der organischen Chemie, Volume 5, Makromolekulare Stoffe, Georg-Thieme Verlag, Stuttgart, 1961, pages 192 to 208.

Alternative surfactants include functional monomers, polymerizable surfactants and water-soluble surface-active polymers, including block copolymers. Specific examples include polyvinyl alcohols, cellulose derivatives or vinylpyrrolidone-containing copolymers. A detailed description of further suitable protective colloids is given in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe, Georg-Thieme-Verlag, Stuttgart, 1961, pages 411 to 420. Currently commercially available surfactants that are useful in this invention are listed below in Table 1.

Table 1:

Trade Name	Supplier	Contents
<b>Ionics</b>		
Abex VA-50	Rhodia	46%; 1:1 mix of anionic and ethoxylated octyl phenol
Abex 2020	Rhodia	Anionic/non-ionic mix (APE free), 30%
Abex 2030	Rhodia	Anionic/non-ionic mix (APE free), 30%
Abex 18-S	Rhodia	Na Ether Sulfates; APE-free, 35%
Abex 12-S	Rhodia	Na Ether Sulfates; APE-free, 30%
Aerosol OT	Sigma	[(Bis-2-ethylhexyl)sodium sulfosuccinate, C <sub>20</sub> H <sub>37</sub> O <sub>7</sub> S.Na, M <sub>w</sub> 444.6, 10%
Aerosol 22	Sigma	[(Bis-2-ethylhexyl)sodium sulfosuccinate, C <sub>20</sub> H <sub>37</sub> O <sub>7</sub> S.Na, M <sub>w</sub> 444.6, neat d=1.12
Calfax DB-45	Pilot Chemical	C <sub>12</sub> (branched) Sodium diphenyloxide disulfonate, 45%
Calfax 16L-35	Pilot Chemical	C <sub>16</sub> (linear) Sodium diphenyloxide disulfonate, 35%
Calimulse L-30	Pilot Chemical	Sodium linear alkyl benzene sulfonate 30%
Calimulse EM-30	Pilot Chemical	Sodium branched dodecyl benzene sulfonate 30%
Calsoft F-90	Pilot Chemical	Sodium linear alkyl benzene sulfonate, solid, 90+%
Dowfax C6L	Dow	Disulfonated diphenyloxide with C <sub>6</sub> backbone
Dowfax C10L	Dow	Disulfonated diphenyloxide with C <sub>10</sub> backbone

accelerators include acetic acid, acetic anhydride, camphor sulfonic acid, acetole (1-hydroxyacetone) and the like. Other accelerators useful herein are recited in Hawker et al., "Development of a New Class of Rate-Accelerating Additives for Nitroxide-Mediated 'Living' Free Radical Polymerization," *Tetrahedron*, Vol. 53, No. 45, pp. 15225-15236 5 (1997), which is incorporated herein by reference. A second, related, method for increasing the rate of polymerization in these living-type systems, it has been found, is to lower the pH of the polymerization system by the addition of an acid to the system. Any compatible acid may be used including organic acids, inorganic acids, Lewis acids and Bronsted acids. Preferred acids include acetic acid, sulfuric acid, methane sulfonic acid, p-toluene sulfonic 10 acid, and polymerizable acids such as acrylic acid, methacrylic acid, and 2-acrylamido-2-methylpropanesulfonic acid (AMPS). The pH can be lowered to about 5 or below for an accelerated polymerization reaction, depending on the exact nitroxide radical used. In other embodiments, the pH is about 4 or lower or about 3.5 or lower.

## 15 Polymerization Systems

The polymerization systems of this invention are combinations or mixtures of components, which include water, control agent, initiating radical and at least one monomer. The addition of a surfactant to the polymerization system is optional, but typically preferred for the emulsion embodiments of this invention. In embodiments that employ the adducts of 20 this invention, the adduct can be thought of as combining the structures and functions of the initiating radical and control agent. The polymerization system is subjected to polymerization conditions to effect polymerization of the at least one monomer. At least one monomer is added to the polymerization system. For random copolymers or higher order interpolymers, two or more monomers may be added to the polymerization system at the same time. For block copolymers, the monomers are typically added in a desired sequence in 25 order to grow the desired block. For the emulsion polymerization systems, the polymerization system is considered to be the starting components, which are subjected to the polymerization conditions. The products of such polymerization systems are the emulsions themselves or the polymers, after drying. For the aqueous solution polymerizations, the 30 polymerization system is typically the combination or mixture of water, control agent, initiating radical and at least one monomer, where the components of the polymerization

may be in the range of from 0.001% to about 90% by volume. In some preferred applications, the novel aqueous polymer emulsions are produced with a solids content of = 40, advantageously = 50%, by volume, based on the total aqueous polymer emulsion. The useful solids content for other applications is from 0.5 to 95% by volume. The preparation of 5 the novel aqueous polymer emulsions is carried out according to the product by process definition of the subject according to the invention, as stated at the outset, *i.e.*, by the free radical aqueous emulsion polymerization method in the presence of dispersants and free radical polymerization initiators. The ratio of the aqueous phase to the total amount of the monomers used in both stages is chosen according to the desired solids content of the 10 aqueous polymer emulsion to be prepared.

Polymerization conditions include the ratio of components, temperature, pressure, atmosphere, reaction time and other conditions generally known to those of skill in the art. Polymerization temperature can range from about -40°C to about 300°C, preferably between about 0°C and about 200°C, more preferably between about 25°C and about 150°C, and most 15 preferably between about 40°C and about 110°C. Alternatively, the temperature may be between about -40° C and 250°C. In other preferred embodiments, the temperature of the polymerization system is controlled to a temperature of less than or equal to about 110°C, more preferably less than or equal to about 100°C, even more preferably less than or equal to about 95°C and for some embodiments less than or equal to about 90°C. This lower 20 temperature embodiment is may possible, in part, due to the preferred nitroxide radical control agents having a destabilizing mechanism available, as discussed in detail above. More preferred is a polymerization temperature below about 100°C and even more preferable below about 95°C. Polymerization conditions also include a pressure between about ambient pressure up to about 100 atmospheres. The atmosphere above the emulsion may also be one 25 of the polymerization conditions, and the atmosphere may be air, nitrogen, argon or another suitable atmosphere. Polymerization conditions also include the time for reaction, which may be from about 0.5 hours to about 72 hours, preferably in the range of from about 1 hour to about 24 hours, more preferably in the range of from about 2 hours to about 12 hours.

Property	Traditional Emulsion	Mini Emulsion	Micro Emulsion	Suspension	Dispersion
Importance of agitation	Moderate to low	high (at start)	Low	high	High
Typical resulting particle size	10 to 200 nm	50 to 500 nm	10 to 100 nm	500 to 5000 nm	500 to 5000 nm
Typical particle size distribution	Narrow	Broad	Narrow	broad	Broad
Typical amount of surfactant (relative to monomer)	0 to 5 %	0.1 to 10 %	≈ 100%	0 to 5 %	0 to 5 %
Thermodynamic stability of particles before polymerization	not stable	not stable	Stable	not stable	Not stable
Typical maximum solids content	50 %	20 %	< 10 %	40 to 50 %	40 to 50 %

Some of these ranges are subjective and extremes may often only be obtained in exceptional circumstances. Terms such as low, medium and high are subjective, and are intended to illustrate differences in the classifications known to those skilled in the art. The processes of the invention are distinguished as discussed herein.

One specifically preferred embodiment of the invention is a controlled heterogenous polymerization reaction in an emulsion characterized by particle sizes ranging from 10 to 150 nm, and preferably from 15 to 100 nm or from 20 to 70 nm in hydrodynamic radius. Polymerizations of this embodiment may have process parameters similar to those discussed above for "traditional" or "true" emulsion polymerizations. These emulsions are stable (on the order of many months with no observed coagulation or sedimentation, yet are prepared using surfactant in amounts less than 2 % by weight to monomer. These emulsions feature a uniform distribution of particle sizes (nonuniformity of the polymer particle radius distribution -- e.g., R.M.S. variation in average polymer particle radius of less than about 50%).

The controlled particle sizes that characterize the controlled polymer emulsions of some embodiments of the invention provide a number of benefits in many applications. The living nature of the polymerization processes of the invention allow for novel means for controlling particle size and distribution of the resulting polymer emulsions. Emulsions of smaller particles are generally very stable and have useful process advantages such as faster

≥ 50,000, or even ≥ 100,000), often with narrow molecular weight distribution (polydispersity ( $M_w/M_N$ ) generally less than 2 and preferably between 1.1 and 1.8, also below 1.4). Likewise, nitroxide control agents provide significant control of particle sizes. While typical particle sizes for uncontrolled radical emulsion polymerizations range from 50  
5 to about 200 nm depending on the amount of monomer and surfactant, polymerizations of the invention have been shown to provide emulsions with smaller particle size, under similar condition of surfactant and monomer concentration. For example, uncontrolled emulsion polymerizations of styrene (1% surfactant, 20% solids and target  $M_w$  of 100,000) yield particle sizes that range from about 50 to about 75 nm radius. By contrast, the emulsion  
10 polymerization processes of this invention with loaded seed can readily produce emulsion polymers with particle sizes less than 40 nm.

In the emulsion polymerization process of this invention, the control agent in radical form is combined with water, surfactant, initiator (or initiating radical), at least one monomer and optionally an accelerator and/or a reagent to react with the control agent under  
15 polymerization conditions. Emulsion polymerization conditions include those discussed above, but most preferably are at a temperature below about 95°C.

### Seeded Emulsion Polymerization Systems

The use of seeds in the controlled emulsion polymerization systems of this invention  
20 may be an important method for controlling the particle nucleation process, number of particles formed, particle size of the final emulsion, and minimizing the amount of coagulum formed in the polymerization. In particular, the use of a seed helps to better control the nucleation step by separating it from the controlled radical polymerization process and thus helps control the final particle size using conventional radical emulsion processes. With  
25 polymerization systems that have living kinetics, this invention provides methods for both achieving a desired particle size with a desired number of chains per particle and a desired molecular weight of those chains, factors that are generally difficult to control separately in conventional radical polymerization processes. In conventional radical emulsion polymerization, surfactant micelles typically provide a locus for polymerization and particle  
30 nucleation, because of the rapid growth of the first few polymerizing chains introduced into the system. However, with the slower chain-growth as compared to uncontrolled

discussed in detail below, the seed typically comprises polymer chains that cannot be further grown or propagated in a polymerization system and/or "living" oligomers, as well as or alternatively other components. In those embodiments where one or more components of the seed may be further grown or propagated in a polymerization system, the seed is referred to  
5 herein as a "loaded seed."

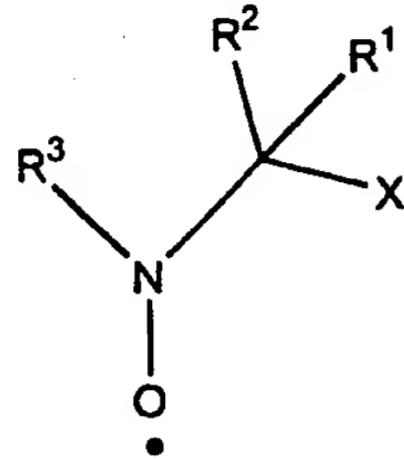
One embodiment of the seeded processes of this invention takes advantage of the living type kinetics of the polymerization systems of this invention (including the ability to re-initiate chains) by supplying the monomer to the system in at least two stages. In the first stage, a seed is made. Depending on the embodiment of the invention being practiced, the  
10 second step is optional, and, comprises loading the seed with either (1) a composition comprised of initiator or initiating radical and/or a control agent or (2) initiator-control agent adduct. The third stage or step is to polymerize a heterogeneous mixture comprising the loaded seed under polymerization conditions. In other embodiments, this process can be described as forming a first mixture comprised of a first polymerizable monomer, initiator,  
15 water and surfactant, wherein said first polymerizable monomer comprises no more than about 10% by weight of said first mixture; subjecting said first mixture to polymerization conditions to give a first heterogeneous polymerization; ending said first heterogeneous polymerization to provide a seed, and optionally recovering said seed; forming a second mixture comprised of said seed, water and either (1) a composition comprised of an initiator or initiating radical and/or a control agent or (2) an initiator-control agent adduct; optionally maintaining the second mixture for a sufficient time under appropriate conditions for either of the composition or adduct to migrate into the seed; forming a third mixture comprised of the second mixture, optionally additional water and/or surfactant and at least one monomer, which may be the same or different from the first polymerizable monomer; and subjecting the  
20 third mixture to polymerization conditions to polymerize the at least one monomer. This third mixture is typically a living type polymerization system. In this alternative description, the first mixture forms the seed, the second mixture loads the seed and the third mixture is the heterogeneous polymerization using the loaded seed. Unloaded seeds may be provided in a manner known to those of skill in the art, such as by uncontrolled polymerization to the  
25 desired seed size, using one or more monomers of choice. In some embodiments it may be desirable to add all of the desired surfactant for the polymerization system in the process to  
30

may be recovered from the polymerization system used to make the seed if the seed is redispersible in a polymerization system or may be used without recovery from the polymerization system. The monomer used for the seed depends on the type of dead polymer chains that the emulsion application can tolerate. In some embodiments, the seed monomer is 5 selected from the group consisting of styrene, tert-butyl acrylamide, styrene sulfonate, etc.

Loaded seeds may be prepared by a choice of methods. In one embodiment, water, surfactant, control agent and initiator are mixed with a fraction of the total desired amount of monomer. This first combination is mixed for a predetermined period of time at a predetermined temperature. Since the amount of monomer is limited, the polymerization 10 reaction proceeds until the monomer is used up, effectively creating at least some "living" oligomers that can be re-initiated (for example, the living oligomers may be characterized by formula VIII, discussed below). Longer dead polymer chains might also be created in this procedure, depending on the conditions chosen. In this manner, an otherwise slow initiator is given the time it needs to initiate as many chains as it can and an organic soluble initiator 15 cannot cause polymerization outside of the desired control mechanism. The amount of time and/or the temperature for this first step is chosen so that the chosen initiator is substantially completely reacted prior to the second or subsequent steps of the polymerization process. In this embodiment, the seeds are loaded in situ with the living oligomers, which then polymerize the remainder of the same or different monomer, which is added in the second 20 step and essentially re-initiates the propagation step. Additional steps can be added for different monomers (to create block copolymers, such as di-block, tri-block or higher order block polymers).

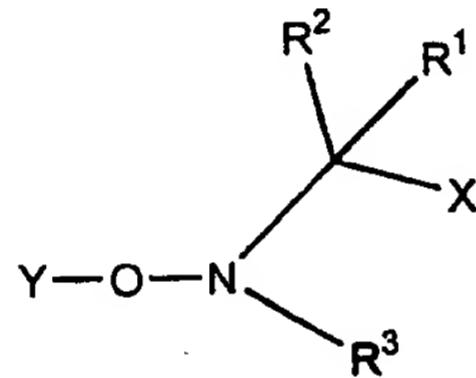
An alternative method for loading seeds is to first polymerize the seed and then load the seed in a second step. Those of skill in the art, as discussed above, generally know about 25 the polymerization of the seed. Whether the seed is recovered from the polymerization system or not, the loading of prepared seeds proceeds by forming a loading system, which comprises a mixture of the seed with either (1) a composition comprised of an initiator, initiating radical and/or control agent or (2) an initiator-control agent adduct in water. In this embodiment, with the composition or adduct should desire to reside in the organic 30 environment of the seed as opposed to the aqueous environment. Thus, the composition or adduct typically will be selected to have greater solubility in the seed than the water. In some

composition comprised of initiating radical and/or control agent or (2) an initiator-control agent adduct. In other embodiments, a loaded seed comprises polymer chains that are unreactive in a free radical polymerization system; and a composition comprised of initiating radical and control agent said control agent being characterized by the general formula:



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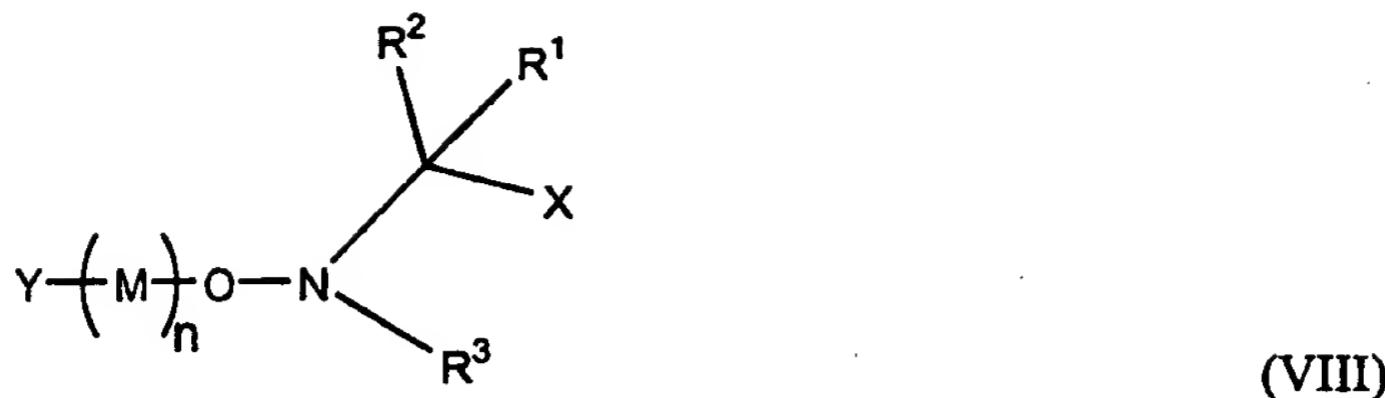
where X, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are defined above. In still other embodiments, the loaded seeds comprise polymer chains that are generally un-reactive in a free radical polymerization; and an initiator-control agent adduct, said initiator-control agent adduct being characterized by the general formula:



10

where X, Y, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are defined above. In still further embodiments, the loaded seeds will comprise the "living" oligomers characterized by formula VIII, below, where n is a relative low integer, such as between about 5 and 100. After the seed is loaded, the loaded seed may be recovered by separating the loaded seed from the loading system, such as by 15 drying the solvent in loading system or with other methods as are known to those of skill in the art.

The loaded seed is subsequently used in the emulsion polymerization system. If the loaded seed is not recovered from the loading system, then the loading system (e.g., the second mixture) is used in a third mixture, the polymerization system. The polymerization 20 system comprises additional one or more monomers and optionally more water. The monomer may be added to the polymerization system all at once or drop wise or otherwise in a controlled fashion. Also, the additional monomer may be the same or different from the monomer used to form the seed. The polymerization system is placed under polymerization



where  $R^1$ ,  $R^2$ ,  $R^3$  and  $X$  have the above meanings, and  $Y$  is a residue derived from a species that initiates free radical polymerization (as discussed above) and may be selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, heteroalkyl,

- 5      substituted heteroalkyl, aryl, and substituted aryl ( $Y$  may also be derived from the list of initiators discussed above);  $M$  is one or more monomers (as discussed above) and may be selected from the group consisting of styrene, substituted styrene, alkyl acrylate, substituted alkyl acrylate, alkyl methacrylate, substituted alkyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, N-alkylacrylamide, N-alkylmethacrylamide, N,N-dialkylacrylamide, N,N-dialkylmethacrylamide, isoprene, butadiene, ethylene, vinyl acetate and combinations thereof; and  $n$  is an integer greater than 1, preferably greater than 10, also preferably greater than 100. As discussed above, these oligomers or polymers may be in emulsion, water-soluble or a loaded seed.

The polymers shown in formula VIII show the nitroxide radical and  $Y$  residue at each 15 end of the polymer. These end groups may be removed or modified as is known to those of skill in the art. Specific methods that may be used include reduction with ascorbate or tin hydrides to replace the nitroxyl group with a hydrogen, addition of other radical species (such as halogens or sulfur species), and destruction of free nitroxide radical to force coupling of chains.

- 20      The living nature of the polymerization processes of this invention provide those of skill in the art the ability to create virtually any type of polymer architecture desired as well as selection from a wide variety of monomers. Thus, this invention includes novel block copolymers of styrene and acrylic acid; styrene and acrylamides (such as t-butyl acrylamide and dimethyl acrylamide); styrene and acrylates (such as n-butyl acrylate and ethyl acrylate);
- 25      styrene and methacrylates (such as n-butyl methacrylate and methyl methacrylate); acrylic acid and methacrylic acid; acrylic acid and acrylamides; acrylic acid and acrylates; acrylic acid and methacrylates; methacrylic acid and acrylamides; methacrylic acid and acrylates;

block can vary in composition or size with respect to the overall block copolymer. In some embodiments, for example, the random block R will account for between 5 and 80 % by weight of the mass of the block copolymer. In other embodiments, the random block R will account for more or less of the mass of the block copolymer, depending on the application.

- 5 Furthermore, the random block may have a compositional gradient of one monomer to the other (e.g., A:B) that varies across the random block in an algorithmic fashion, with such algorithm being either linear having a desired slope, exponential having a desired exponent (such as a number from 0.1-5) or logarithmic. The random block may be subject to the same kinetic effects, such as composition draft, that would be present in any other radical copolymerization and its composition, and size may be affected by such kinetics, such as Markov kinetics. For example, as shown below in the examples, a block copolymer of (random methyl methacrylate-ureidoethylmethacrylate) and styrene is made that is within the scope of this definition. Any of the monomers listed elsewhere in this specification may be used in the block copolymers of this invention.
- 10
- 15 A "block" within the scope of the block copolymers of this invention typically comprises about 10 or more monomers of a single type (with the random blocks being defined by composition and/or weight percent, as described above). In preferred embodiments, the number of monomers within a single block may be about 15 or more, about 20 or more or about 50 or more. However, in an alternative embodiment, the block copolymers of this invention include blocks where a block is defined as two or more monomers that are not represented elsewhere in the copolymer. This definition is intended to encompass adding small amounts of a second monomer at one or both ends of a substantially homopolymeric polymer. In this alternative embodiment, the same copolymer architectures discussed above apply. This definition is therefore intended to include telechelic polymers,
- 20
- 25 which include one or more functional end groups capable of reacting with other molecules. Thus, generally, a telechelic polymer is a block copolymer with in the definitions of this invention. The functional groups present at one or both ends of a telechelic polymer may be those known to those of skill in the art, including, for example, hydroxide, aldehyde, carboxylic acid or carboxylate, halogen, amine and the like, which have the ability to
- 30
- associate or form bonds with another molecule. Likewise, the block copolymers of the invention are intended to encompass telechelic polymers containing bifunctional groups, such

higher reaction rates) until the remaining monomer is consumed. Block copolymer can also be created by grafting monomers, monomer mixtures, oligomers or polymers only polymers having multiple available functional groups.

In other embodiments, block copolymers can be prepared by grafting processes, 5 preparation of telechelic polymers, preparation of macromonomers, etc. In these embodiments, at least one polymer segment is derived from a living or controlled process of the invention, while other segments can be derived from any polymerization process, including, for example, controlled or uncontrolled radical polymerization, condensation polymerization, ionic polymerization, surface modification or grafting, or other addition or 10 step-growth processes.

The combination of heterogeneous (and particularly emulsion) conditions with living-type free radical kinetics provides a high degree of control over the composition, architecture, phase morphology and microstructure of polymers produced according to the invention. These methods may be practiced to form new polymers, including, for example, di-, tri-, 15 poly-, multi-arm, star and graft block copolymers in addition to novel homopolymers.

Block copolymers allow the combination of potentially diverse polymer properties (such as hard/soft and/or hydrophilic/hydrophobic (amphiphilic) blocks) into a single polymer chain. Hard/soft block copolymers combine segments with significantly different glass transition temperatures  $T_g$ . A typical hard/soft copolymer pairs a relatively "hard" 20 block (e.g., styrene) with a relatively "soft" block (e.g., butyl acrylate). The resulting materials can possess performance attributes not found in any of the constituent segments. The presence of microphase separation and various phase morphologies in block copolymers is associated with unique performance attributes of many block copolymers. For example, by combining the stiffness or rigidity characteristic of hard materials with the compliance of soft 25 materials, block copolymers may exhibit advantageous properties, such as processability under melt conditions, elasticity, resistance to abrasion and cracking and desired creep characteristics (corresponding to the material's ability to hold its shape under external stresses) depending on morphology, making them appropriate for use as extrudable bulk materials, coatings and separation media. The exact properties of a hard/soft copolymer 30 depend significantly on the difference between the glass transition temperatures of the constituent blocks; accordingly, selection of monomers having glass transition temperatures a

typically in the range 10-100 nm. Such microphase separation can be detected obtained in a variety of ways, including electron microscopy, x-ray or neutron scattering or reflectivity, measurement of optical anisotropy, and rheological measurements. The absence of a periodic microstructure is not necessarily evidence against having synthesized a block copolymer, as such absence may be due to low molecular weight, weak intermolecular interactions, or inadequate time and slow kinetics for microphase separation. However, the presence of a periodic microstructure on the 10-100 nm scale is considered extremely compelling evidence for block copolymer formation in accord with this invention.

Block copolymers are well-known to form terraced films, where the film thickness is restricted to integer or half-integer multiples of the microstructure period. This occurs because preferential interactions of one or the other block with the substrate and/or free surface cause a layering of the microdomains parallel to the film surface (see for example G. Coulon, D. Ausserre, and T.P. Russell, *J. Phys. (Paris)* 51, 777 (1990); and T.P. Russell, G. Coulon, V.R. Deline, and D.C. Miller, *Macromolecules* 22, 4600-6 (1989)). When observed in a reflection microscope (on a reflecting substrate such as a silicon wafer), the terracing manifests itself as a series of discrete, well-defined colors with sharp boundaries between them as shown in FIG. 12. The colors are a result of interference between light reflected from the top and bottom surfaces of the film, and depend on the local film thickness ("Newton's rings"). If terracing does not occur, the colors blend continuously from one into the other.

The presence of block copolymer can also be determined using transmission electron microscopy as illustrated in FIGS. 13A and 13B.

The novel properties of the copolymers and emulsions, including the high molecular weight, low polydispersity and controlled phase morphology and microstructure of the copolymers and the particle size and optical purity of the emulsions make them suitable for a wide variety of applications including adhesives, binders, coatings, dispersants, scavengers, rheology modifiers, bulk extrudable materials and health and personal care products. Thus, for example, pressure sensitive adhesives may be prepared using the emulsions or dispersions of this invention, with such adhesives including tackifiers and/or plasticizers, as known in the art (see, e.g., U.S. Patent No. 4,879,333, which is incorporated herein by reference).

phosphomolydic acid hydrate in EtOH with heating. Gas chromatography/mass spectrometry (GC/MS) was performed using an HP 6890 gas chromatograph equipped with an automatic injector, a siloxane-coated capillary column, and an HP 5973 mass spectrometer. Second cumulant analysis PDI was determined as discussed above. Mp refers to peak molecular weight as determined by SEC.

**Example 1: Preparation of Nitroxide Radicals, Starting Materials and Initiator-  
Control Agent Adducts.**

This example provides methods of synthesizing nitroxide radicals, starting materials and initiator control agent adducts that are useful in this invention. Part A shows the source or preparation of starting nitrones. Part B shows conversion of nitrones into nitroxide radicals. Parts C, D and E show preparation of molecules that are used in the preparation of initiator control agent adducts, which is shown in detail in Part F. Parts G, H, I and J show conversion of initiator control agent adducts (some of which are from Part F) into different initiator control agent adducts. Part K shows preparation of the hydroxyl functionalized initiator control agent adducts.

**PART A**

**20 Synthesis of *N-t*Bu, $\alpha$ -Arylnitrones:**

The following Scheme 1 was followed, in connection with Table 3:

Scheme 1:

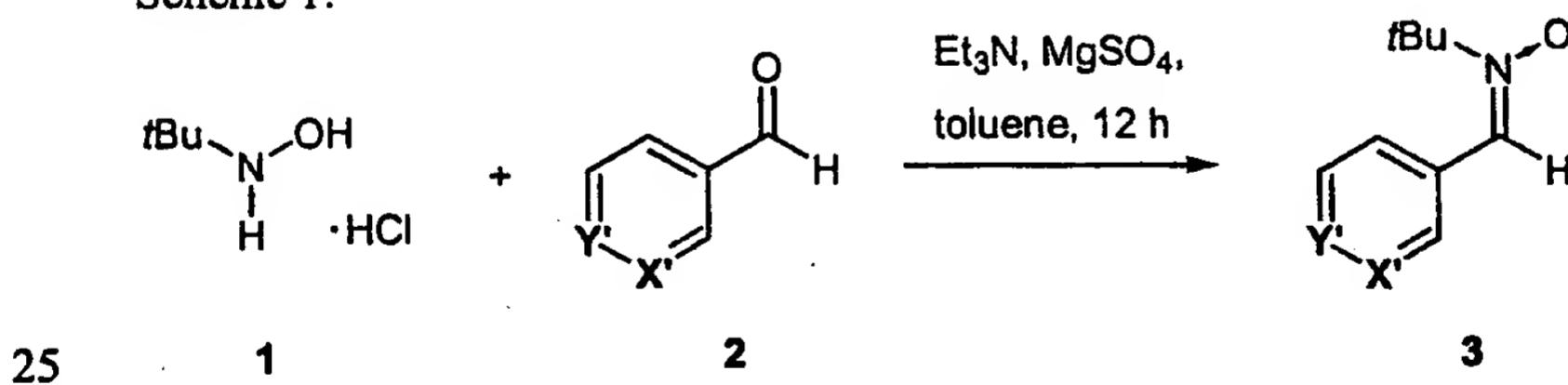


Table 3:

Entry	Aldehyde 2	Nitrone 3	X'	Y'	yield [%]
1	2a	3a	CH	CH	commercially available
2	2b	3b	N	CH	84 %
3	2c	3c	CH	CBr	quant.

yellow oil by column chromatography (silica gel, EtOAc/hexanes = 1:6 to 1:3) yielded 8.95 g (quant.) of colorless crystals.  $R_f$ : 0.25 (EtOAc/hexanes = 1:4, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  8.14 (dt,  $J$  = 8.7, 2.4 Hz, 2H, Ar-H), 7.49 (dt, superimposed,  $J$  = 8.7, 2.4 Hz, 2H, Ar-H), 7.48 (s, superimposed, 1H, HC(=N)), 1.56 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  131.53, 130.06, 129.81, 128.92, 123.73, 71.09, 28.20 ppm.

## PART B

## 10 Synthesis of 4-aryl, 3-oxyl, 2,2,5-trimethyl-3-azahexanes:

The following Scheme 2 was followed in connection with Table 4:

Scheme 2:

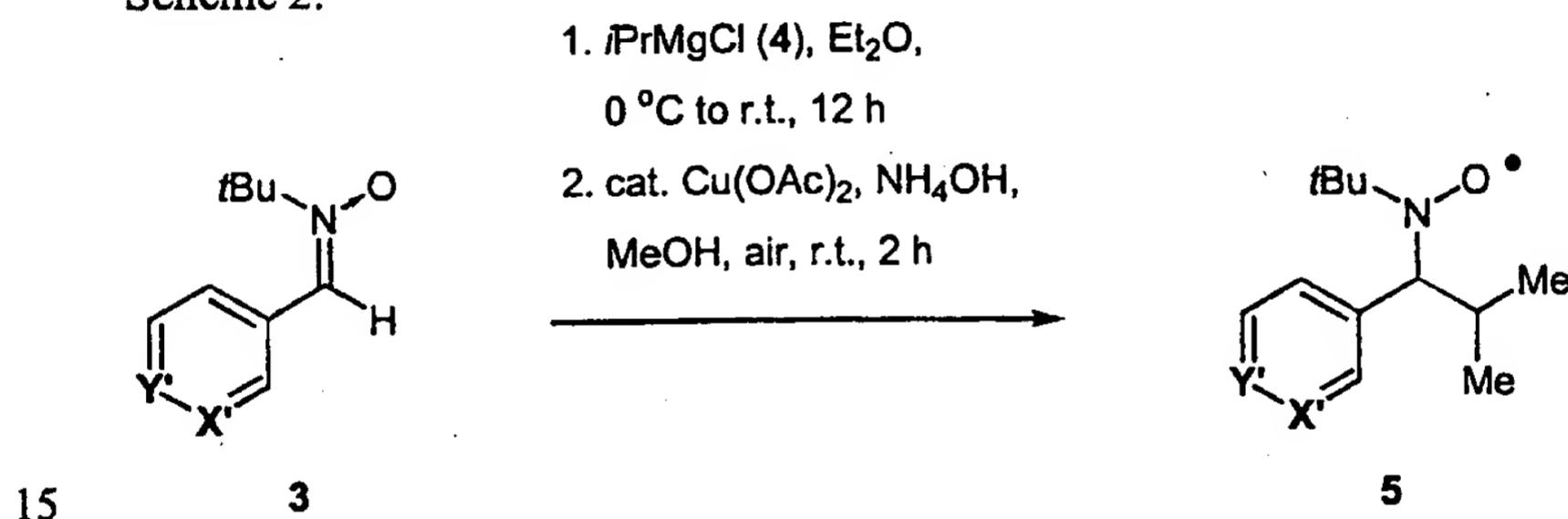


Table 4:

Entry	nitrone 3	Nitroxide 5	X'	Y'	yield [%]
1	3a	5a	CH	CH	ca. 90
2	3b	5b	N	CH	ca. 90
3	3c	5c	CH	Br	56

### Synthesis of nitroxide 5a:

An oven-dried 500 mL Schlenk-flask equipped with a magnetic stirring bar and a rubber septum was charged under argon atmosphere with 8.86 g (50.0 mmol) of *N*-*tert*-Butyl- $\alpha$ -phenylnitrone (**3a**). The compound was dissolved in 250 mL of anhydrous THF at room temperature. The yellowish solution was cooled to 0 °C (ice bath) and isopropylmagnesium chloride (**4**) (2 M in THF, 40 mL, 80.0 mmol) were added dropwise at this temperature with a syringe. The reaction mixture was stirred overnight with warming to room temperature to

isopropylmagnesium chloride (**4**) (2 M in THF, 5.0 mL, 10.0 mmol) in 50 mL of anhydrous tetrahydrofuran (THF). Both, t.l.c. and GC/MS ( $M^+ = 222$ ) showed formation of the intermediate hydroxylamine. After work-up, oxidation of the crude intermediate hydroxylamine in 50 mL of MeOH and 5.0 mL of 28 % aq. NH<sub>4</sub>OH (some precipitation of Mg(OH)<sub>2</sub> occurred) and in the presence 46 mg of Cu(OAc)<sub>2</sub> yielded 995 mg (ca. 90 %) of the crude nitroxide as a dark orange oil. Both, t.l.c. and GC/MS ( $M^+ = 221$ ) showed that the crude product contained some impurity of the nitrone ( $M^+ = 220$ ) due to overoxidation of nitroxide in a ratio of ca. 10:1 in favor for the nitroxide. The crude product was directly used in the next step without further purification.

10

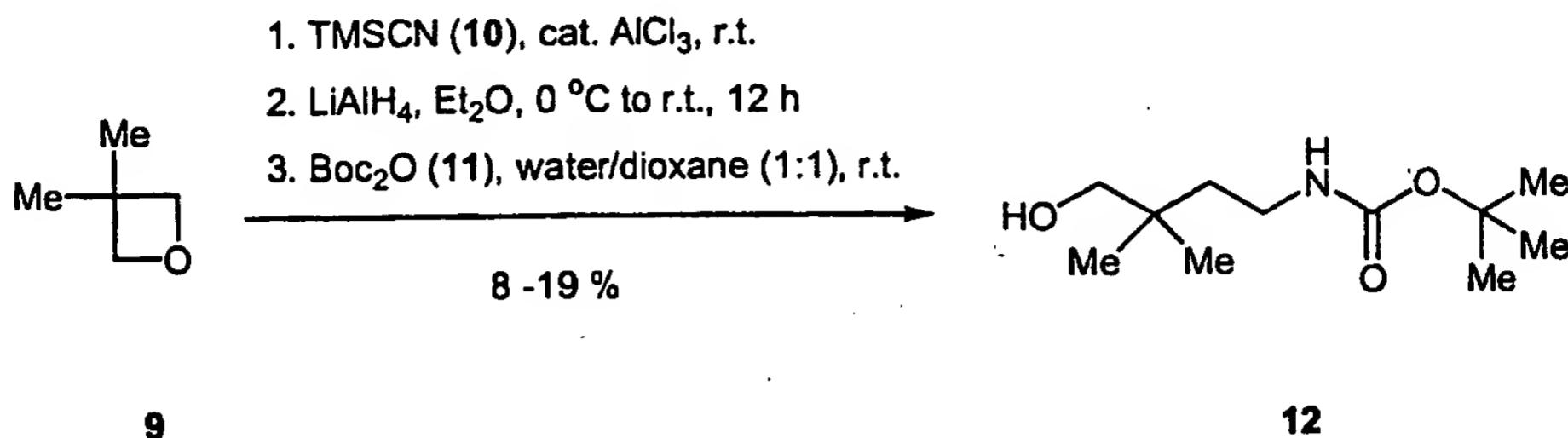
**Synthesis of nitroxide **5c**:**

By analogy for the procedure for the synthesis described above, nitroxide **5c** was prepared from *N*-*tert*-butyl- $\alpha$ -(3-pyridyl)nitrone (**3c**) (8.96 g, 35.0 mmol) and isopropylmagnesium chloride (**4**) (2 M in THF, 35.0 mL, 70.0 mmol) in 250 mL of anhydrous tetrahydrofuran (THF). T.l.c. showed clean formation of the intermediate hydroxylamine. After work-up, oxidation of the crude intermediate hydroxylamine in 250 mL of MeOH and 25.0 mL of 28 % aq. NH<sub>4</sub>OH and in the presence of 317 mg (1.75 mmol) of Cu(OAc)<sub>2</sub> yielded the crude nitroxide as a dark orange oil which solidified upon standing at room temp. Purification by medium pressure liquid chromatography (MPLC) (silica gel, EtOAc/hexanes = 1:24) yielded 5.85 g (56 %) of a bright orange crystalline solid. The purified product was then used in the next step.  $R_f$ : 0.48 (EtOAc/hexanes = 1:9).

**PART C****25      Synthesis of Dimethyl (5-ethylenyl)isophthalate:**

The following Scheme 3 was following in this part:

**Scheme 3:**



**Synthesis of the Neon-B protecting group:**

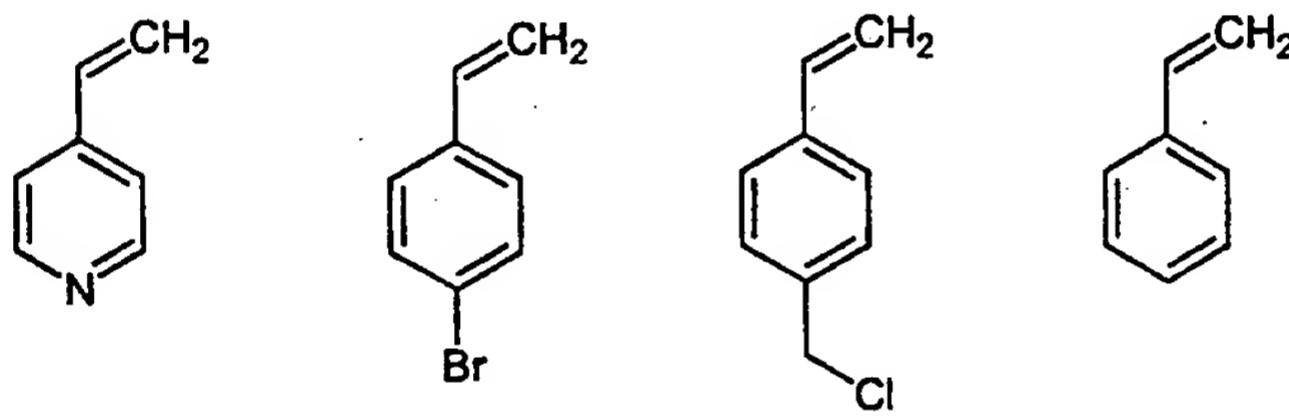
According to the protocol of J.C. Roberts, *et al.* (*Tetrahedron Lett.*, 1997, 38, 355-358; 5 WO 96/18609), an oven-dried 100 mL Schlenk flask equipped with a magnetic stir bar and a rubber septum was loaded under an atmosphere of argon and at room temp. with 9.86 g (100 mmol, 13.5 mL) trimethylsilylcyanide (10) followed by 269 mg (2.0 mmol) of aluminum trichloride to yield a colorless jelly. 8.35 g (97 mmol) 3,3-dimethyloxetane (9) were added at room temp. and the reaction mixture was stirred for 12 h at room temp. Unhydrous diethyl ether (100 mL) was added to the nitrile, the solution was cooled to ca. 0 °C (ice bath) and 240 mL of a 1.0 M LiAlH<sub>4</sub>-solution in diethyl ether (240 mmol) were added dropwise. Upon warming to room temp., the reaction mixture was stirred for 12 h, and excess reduction reagent was quenched by successive careful addition of 10 mL water, 10 mL of 5 % aq. NaOH-solution, and 10 mL water. The colorless Al-containing precipitate was filtered off 10 through a sintered glass-funnel, washed with diethyl ether (2 x 50 mL) and the solvent was evaporated under reduced pressure to yield a pale yellow oil which was used directly without further purification in the next step. The crude product was dissolved in dioxane (50 mL) and 15 ca. 16.2 mL of 6.0 N hydrochloric acid were added (formation of amine hydrochloride). After 30 min. at room temp., the pH of the reaction mixture was adjusted to about 8.0 (pH-paper) by slow addition of a saturated aq. NaHCO<sub>3</sub>-solution, and the reaction mixture was 20 diluted with water (100 mL). Di-*tert*-butyl dicarbonate (Boc<sub>2</sub>O, 11) (24.0 g, 110 mmol) was added portionwise and stirring was continued for 16 h at room temp. After partial concentration under reduced pressure, the concentrate was diluted in EtOAc (150 mL) and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organics were 25 washed with sat. aq. NH<sub>4</sub>Cl-solution, water, brine, dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure to yield a pale yellow oil. Purification by MPLC (EtOAc/hexanes =

= 8:1 to 2:1) yielded 768 mg (40 %) of a colorless viscous oil.  $R_f$ : 0.45 (EtOAc/hexanes = 1:2, 0.3 % aqueous KMnO<sub>4</sub> staining). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  7.81 (d,  $J$  = 8.4 Hz, 2H, Ar-H), 7.52-8.11 (d,  $J$  = 8.4 Hz, 2H, Ar-H), 6.73 (dd,  $J$  = 17.7, 11.1 Hz, 1H, CH=CHH), 5.88 (d,  $J$  = 17.7 Hz, 1H, CH=CHH), 5.44 (d,  $J$  = 17.7 Hz, 1H, CH=CHH), 4.44 (br. s, 1H, NH), 3.66 (s, 2H, CH<sub>2</sub>O), 3.10-2.295 (br. m, 2H, CH<sub>2</sub>CH<sub>2</sub>N), 1.44-1.36 (br. m, s, superimposed, 11H, CH<sub>2</sub>CH<sub>2</sub>N, C(CH<sub>3</sub>)<sub>3</sub>), 0.87 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  155.74, 142.87, 135.10, 134.51, 128.18, 126.78, 118.04, 79.16, 77.91, 38.22, 36.18, 33.58, 28.34, 23.72 ppm.

10

**PART E**

The sources of the following compounds are shown below:



15

**Commercial sources of compounds 15-18:**

- 15:** 4-Vinylpyridine, [100-43-6], Aldrich chemical company, Milwaukee, USA; 100 mL.
- 16:** 4-Bromostyrene, [2039-82-9], Aldrich chemical company, Milwaukee, USA; 25 g.
- 20** **17:** Vinylbenzyl chloride ([4-chloromethyl)styrene], [1592-20-7], Aldrich chemical company, Milwaukee, USA; 100 mL.
- 18:** Styrene, [100-42-5], Aldrich chemical company, Milwaukee, USA; 100 mL.

25

**PART F****Synthesis of Alkoxyamines:**

The following Scheme 6, in connection with Table 5, was followed in this Part F.

butylsalicylidene)-1,2-cyclohexanediaminato) managanese (III) chloride, which is commercially available), and styrene derivative **8** (1.299 g, 5.9 mmol) were added followed by 446 mg (11.8 mmol) of NaBH<sub>4</sub>. Through the dark brown, cloudy reaction mixture was bubbled air for ca. 12 h at room temperature and the reaction mixture was stirred thoroughly.

5 After this time most of the EtOH and toluene were evaporated, residual solvent was removed under reduced pressure. The dark brown residue was diluted with a mixture of EtOAc/hexanes (1:50) (20 mL) and sonicated for several minutes to yield a dark brown suspension which was filtered over silica gel. The filter residue was washed with hexanes and the filtrates were combined. The organics were washed with water and saturated aqueous

10 NaCl-solution, dried over MgSO<sub>4</sub>, filtrated, and evaporated under reduced pressure to yield dark brown viscous oil. The alkoxyamine was eluted from the residue by means of MPLC with EtOAc/hexanes (0:100 to 1:14) to yield 1.385 g (50 %) of a colorless crystalline solid. *R*<sub>f</sub>: 0.29 (EtOAc/hexanes = 1:14, UV<sub>254</sub>-quenching). Under the reaction conditions a transesterification from the methyl ester to the ethyl ester functionality occurred. <sup>1</sup>H NMR

15 (300 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 8.64 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.58 (t, *J* = 1.5 Hz, 1H, Ar-H), 8.33 (d, *J* = 1.5, Hz, 2H, Ar-H), 8.22 (d, *J* = 1.5, Hz, 2H, Ar-H), 7.47-7.40 (br. m, 4H, Ar-H, both diastereoisomers), 7.35-7.12 (br. m, 6H, Ar-H, both diastereoisomers), 5.20 (q, superimposed, *J* = 6.6 Hz, 1H, CHCH<sub>3</sub>), 5.10 (q, superimposed, *J* = 6.6 Hz, 1H, CHCH<sub>3</sub>), 4.53-4.36 (2q, superimposed, *J* = 7.0 Hz, 8H, OCH<sub>2</sub>CH<sub>3</sub>), 3.42 (d, *J* =

20 10.8 Hz, 1H, NCH), 3.28 (d, *J* = 10.5 Hz, 1H, NCH), 2.50-2.20 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.93-1.77 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.68 (d, *J* = 6.6 Hz, 3H, CHCH<sub>3</sub>), 1.59 (d, *J* = 6.6 Hz, 3H, CHCH<sub>3</sub>), 1.42 (t, *J* = 7.0 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, *J* = 7.0 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.24 (d, *J* = 7.2 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.05 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.87 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.53 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.18 (d, *J* = 6.3 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm.

25 <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp., one diastereoisomer): δ 165.86, 146.49, 142.01, 131.50, 130.84, 130.77, 129.10, 127.39, 126.41, 82.70, 72.32, 61.21, 60.48, 31.95, 28.25, 24.30, 21.89, 21.15, 14.26 ppm.

**Synthesis of alkoxyamine 19b:**

30 By analogy to the procedure described above, 128 mg (0.58 mmol) of nitroxide **5a** was reacted in 5 mL EtOH/toluene (1:1) with 222 mg (0.58 mmol) of styrene derivative (**14**) in

9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (d, *J* = 6.3 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.78 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.53 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.25 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 154.24, 153.41, 149.67, 142.00, 141.81, 130.78, 130.60, 127.40, 127.29, 126.44, 126.34, 121.74, 121.05, 82.40, 81.22, 72.16, 72.00, 65.76, 60.59, 5 60.52, 31.98, 31.88, 31.51, 28.31, 28.11, 24.34, 22.93, 22.57, 21.84, 21.72, 20.99, 15.20 ppm.

#### Synthesis of alkoxyamine 19d:

By analogy to the procedure described above, 1.54 g (7.0 mmol) of nitroxide 5a were reacted in 80 mL EtOH/toluene (1:1) with 2.56 g (14.0 mmol, 1.83 mL) of 4-bromostyrene 10 (16) in the presence of Jacobsen's Mn-salen complex (670 mg, 1.05 mmol) and NaBH<sub>4</sub> (0.70 g, 14.0 mmol) to yield 2.77 g (97 %) of a colorless viscous oil after purification by column chromatography (hexanes). *R*<sub>f</sub>: 0.34 (hexanes = 1:4, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 7.51-7.12 (m, superimposed, 18 H, Ar-H, both diastereoisomers), 4.91 (2q, superimposed, *J* = 6.6 Hz, 2H, CHCH<sub>3</sub>), 3.40 (d, *J* = 10.8 Hz, 1H, NCH), 3.31 (d, *J* = 10.8 Hz, 1H, NCH), 2.39-2.22 (br. m, superimposed, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (d, *J* = 6.6 Hz, 3H, CHCH<sub>3</sub>), 1.51 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.47-1.34 (br. m, superimposed, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.03 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.93 (d, *J* = 5.4 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.76 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.52 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.25 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 144.75, 144.69, 144.19, 143.94, 142.17, 141.98, 131.36, 131.18, 131.15, 130.93, 130.84, 130.74, 129.44, 129.26, 128.57, 127.85, 127.39, 127.24, 126.40, 126.26, 120.97, 120.38, 119.82, 119.59, 82.88, 81.92, 72.17, 60.48, 60.39, 46.49, 45.89, 34.65, 31.98, 31.76, 31.55, 28.38, 28.22, 25.27, 24.56, 23.16, 22.63, 22.03, 21.91, 21.13, 21.07, 20.71, 20.50, 18.55, 14.13 ppm.

25

#### Synthesis of alkoxyamine 19e:

By analogy to the procedure described above, 11.02 g (50.0 mmol) of nitroxide 5a were reacted in 200 mL EtOH/toluene (1:1) with 11.45 g (75.0 mmol, 10.57 mL) of (4-chloromethyl)styrene (17) in the presence of Jacobsen's Mn-salen complex (4.75 g, 7.5 mmol) and NaBH<sub>4</sub> (3.75 g, 100 mmol) to yield 11.00 g (58 %) of a colorless viscous oil after purification by column chromatography (silica gel, hexanes). *R*<sub>f</sub>: 0.34 (hexanes = 1:4, UV<sub>254</sub>-

**Synthesis of alkoxyamine 19g:**

By analogy to the procedure described above, 3.901 g (13.04 mmol) of nitroxide **5c** were reacted in 100 mL EtOH/toluene (1:1) with 2.083 g (20.0 mmol, 2.29 mL) of styrene **(18)** in the presence of Jacobsen's Mn-salen complex (1.242 g, 1.96 mmol) and NaBH<sub>4</sub> (984 mg, 26.1 mmol) to yield 4.670 g (89 %) of a pale yellow viscous oil after purification by MPLC (silica gel, EtOAc/hexanes = 1:100). *R*<sub>f</sub>: 0.26 (EtOAc/hexanes = 1:4, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 7.45-7.12 (m, superimposed, 18 H, Ar-H, both diastereoisomers), 4.90 (q, superimposed, *J* = 6.3 Hz, 1H, CHCH<sub>3</sub>), 4.89 (q, superimposed, *J* = 6.3 Hz, 1H, CHCH<sub>3</sub>), 3.39 (d, *J* = 10.5 Hz, 1H, NCH), 3.27 (d, *J* = 10.8 Hz, 1H, NCH), 2.38-2.20 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.54 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48-1.40-1.28 (br. m, superimposed, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, *J* = 6.6 Hz, 3H, CHCH<sub>3</sub>), 1.05 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.92 (d, *J* = 6.3 Hz, 3H, CHCH<sub>3</sub>), 0.78 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.54 (d, *J* = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.21 (d, *J* = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 145.46, 144.68, 141.50, 141.25, 132.57, 130.50, 130.29, 128.10, 127.41, 126.93, 126.71, 126.08, 120.33, 120.16, 83.53, 82.89, 71.48, 71.38, 60.55, 60.44, 31.95, 31.55, 28.43, 28.24, 24.63, 23.00, 22.03, 21.85, 21.05, 20.93 ppm.

**20      Synthesis of alkoxyamine 19h:**

By analogy to the procedure described above, 1.676 g (5.6 mmol) of nitroxide **5c** were reacted in 600 mL EtOH/toluene (1:1) with 1.537 g (8.4 mmol, 1.1 mL) of 4-bromostyrene **(16)** in the presence of Jacobsen's Mn-salen complex (534 mg, 0.84 mmol) and NaBH<sub>4</sub> (420 mg, 10.2 mmol) to yield 2.652 g (98 %) of a pale yellow viscous oil after purification by MPLC (silica gel, hexanes). *R*<sub>f</sub>: 0.34 (hexanes, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp., both diastereoisomers): δ 7.60-7.11 (m, superimposed, 16 H, Ar-H), 4.92-4.86 (2q, superimposed), 2H, CHCH<sub>3</sub>), 3.42 (d, *J* = 10.5 Hz, 1H, NCN), 3.22 (d, *J* = 10.5 Hz, 1H, NCH), 2.38-2.20 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (d, *J* = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.48-1.30 (br. m, superimposed, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, *J* = 6.0 Hz, 3H, CHCH<sub>3</sub>), 1.07 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.97 (d, *J* = 6.3 Hz, 3H, CHCH<sub>3</sub>), 0.81 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.57 (d, *J* = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.29 (d, *J* = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C

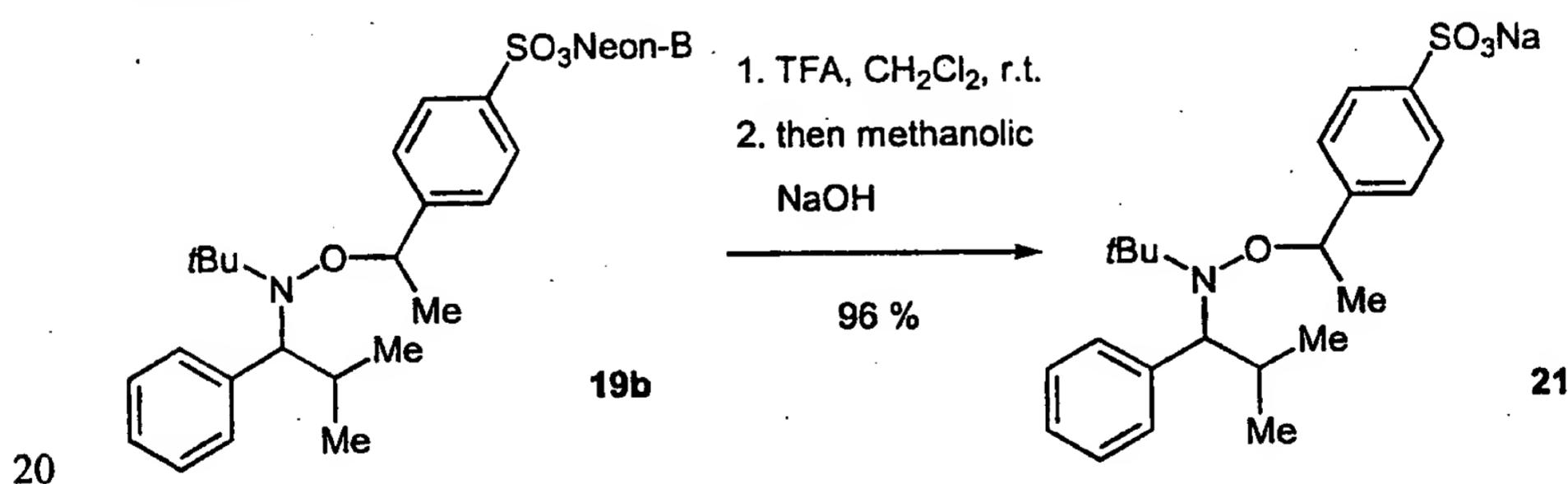
CO<sub>2</sub>H), 8.43 (s, 1H, Ar-H), 8.36 (s, 1H, Ar-H), 8.31 (s, 2H, Ar-H), 8.12 (s, 1H, Ar-H), 5.07 (br. 2q, superimposed, *J* = 6.0 Hz, 2H, CHCH<sub>3</sub>, both diastereoisomers), 3.57 (d, *J* = 10.5 Hz, 1H, NCH), 3.51 (d, *J* = 10.5 Hz, 1H, NCH), 2.4-2.2 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.61 (d, *J* = 6.3 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (d, *J* = 6.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36-1.20 (br. m, superimposed, H, 5 CH(CH<sub>3</sub>)<sub>2</sub>), 1.30 (d, *J* = 6.0 Hz, 3H, CHCH<sub>3</sub>), 1.03 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.82 (d, *J* = 6.3 Hz, 3H, CHCH<sub>3</sub>), 0.72 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.50 (d, *J* = 6.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.13 (d, *J* = 6.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, d<sup>6</sup>-DMSO, room temp., both diastereoisomers): δ 166.65, 146.25, 145.56, 144.85, 141.76, 141.50, 135.67, 133.54, 132.78, 131.93, 131.38, 131.30, 131.20, 131.05, 130.64, 129.21, 128.75, 127.42, 127.20, 126.51, 126.34, 121.96, 10 82.06, 81.26, 71.37, 71.08, 60.31, 60.09, 31.64, 31.28, 28.11, 27.97, 24.05, 22.55, 21.70, 21.64, 20.91, 20.77, 15.33 ppm.

## PART H

### 15 Synthesis of the sulfonate substituted alkoxyamine:

The following Scheme 8 was followed in this part.

Scheme 8:



### Synthesis of the sulfonate substituted alkoxyamine (21):

According to a protocol of J.C. Roberts, *et al.* (*Tetrahedron Lett.* 1997, 38, 355-358; WO 96/18609), an oven-dried 25 mL Schlenk-flask equipped with a magnetic stir bar and a rubber septum was loaded under an atmosphere of argon with 125 mg (0.21 mmol) of alkoxyamine 19b. The compound was dissolved in 4.75 mL of anhydrous MeOH.

An ovendried 100 mL Schlenk-flask equipped with a magnetic stirring bar and a rubber septum was charged under argon atmosphere with 1.19 g (2.96 mmol) the alkoxyamine **19g**. The compound was dissolved in 20 mL of anhydrous diethylether at room temp. The solution was cooled to -78 °C (dryice/isopropanol bath) and 3.83 mL (6.51 mmol) of a 1.7 M 5 solution of *tert*-butyllithium in pentane is added dropwise via a syringe. The reaction mixture turned yellow and was kept at this temperature for ca. 1 hour. A stream of pre-dried (by H<sub>2</sub>SO<sub>4</sub>) carbondioxide was passed through the solution at this temperature. Stirring and gasfeed was continued for additional 3 h with warming to room temperature to yield an almost colorless reaction mixture. The reaction was quenched with 10 mL of water and the 10 aqueous phase was acidified with a 10 % aqueous KHSO<sub>4</sub>-solution. After dilution with diethyl ether and phase separation, the aqueous phase was extracted with diethyl ether (3 x 30 mL). The combined organic extracts were washed with brine (50 mL), dried over MgSO<sub>4</sub>, filtered and the filtrate was evaporated under reduced pressure to yield 1.06 g (97 %) of a colorless solid. <sup>1</sup>H NMR (300 MHz, d<sup>6</sup>-DMSO, room temp., both diastereoisomers): δ 12.65 15 (br. s, 2H, CO<sub>2</sub>H), 7.87 (d, J = 8.4 Hz, 2H, Ar-H), 7.55 (d, J = 8.4 Hz, 2H, Ar-H), 7.65-7.11 (br. m, 14 H, Ar-H, both diastereoisomers), 4.86 (2q, superimposed, 2H, CHCH<sub>3</sub>, both diastereoisomers), 3.53 (d, J = 10.5 Hz, 1H, NCH), 3.40 (d, J = 10.5 Hz, 1H, NCH), 2.36-2.22 (br. m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.55 (d, J = 6.6 Hz, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, J = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.37-1.20 (br. m, superimposed, 4H, CH(CH<sub>3</sub>)<sub>2</sub>, CHCH<sub>3</sub>), 0.99 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 20 0.86 (d, J = 6.3 Hz, 3H, CHCH<sub>3</sub>), 0.73 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 0.47 (d, J = 6.3 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.13 (d, J = 6.6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, d<sup>6</sup>-DMSO, room temp., both diastereoisomers): δ 179.30, 167.40, 167.35, 147.35, 147.15, 144.91, 144.17, 130.79, 128.92, 128.72, 128.35, 128.07, 128.01, 127.44, 126.89, 126.74, 125.89, 82.86, 82.30, 77.20, 72.01, 70.82, 70.70, 60.22, 60.11, 37.65, 35.81, 31.40, 30.94, 28.04, 27.85, 27.66, 24.19, 22.59, 25 21.84, 21.52, 20.61 ppm.

**Synthesis of the lithiosulfonate substituted alkoxyamine **22b**:**

By analogy to the procedure described above, 809 mg (2.0 mmol) of alkoxyamine **19g** were reacted in 20 mL of anhydrous diethyl ether with 2.6 mL of a 1.7 M solution of *tert*-30 butyllithium in pentane. The intermediate lithio derivative of **19g** was reacted at -78 °C with 0.33 g (2.4 mmol) of SO<sub>3</sub>·NMe<sub>3</sub> complex, followed by warming to room temperature to yield a

151.02, 149.94, 149.09, 147.31, 147.09, 130.83, 130.01, 129.42, 129.08, 128.89, 128.52, 128.32, 127.56, 126.98, 126.01, 82.87, 81.92, 70.95, 60.30, 60.22, 37.72, 31.52, 31.29, 31.14, 28.10, 27.90, 27.73, 27.03, 25.48, 24.14, 22.63, 21.78, 21.54, 20.65 ppm.

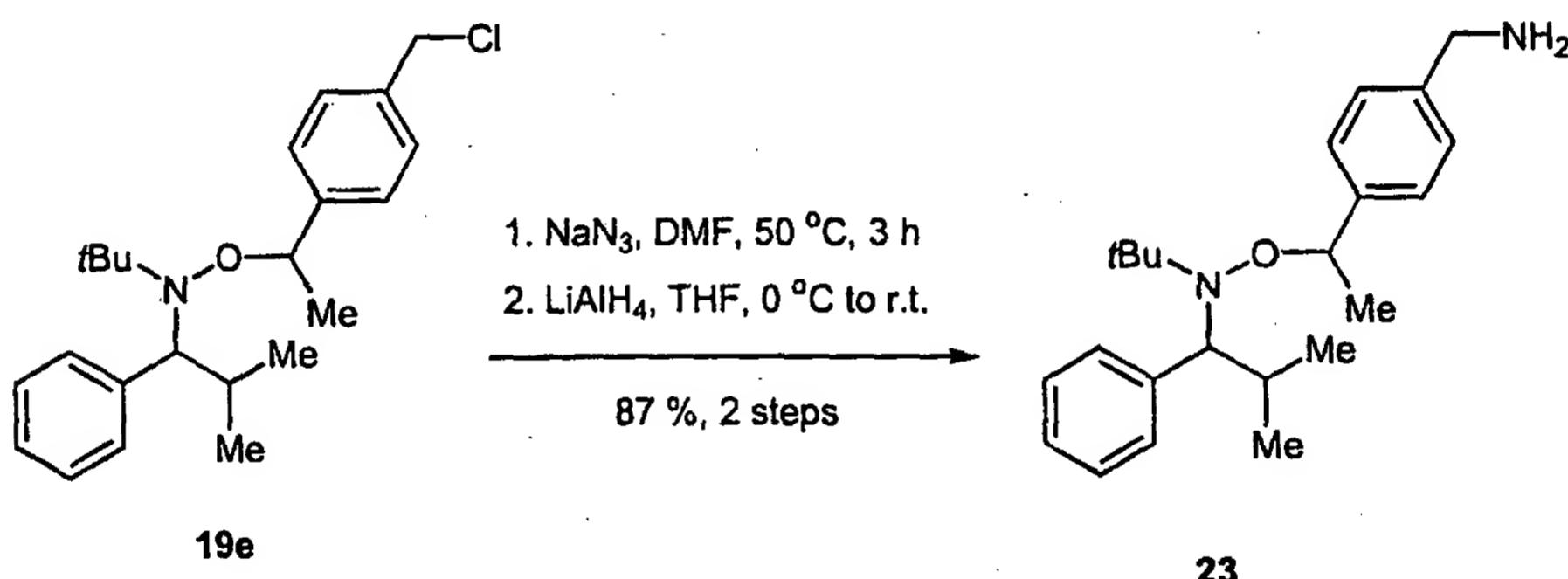
5

**PART J****Synthesis of the aminomethyl-functionalized alkoxyamine:**

The following Scheme 10 was followed in this part.

10

Scheme 10:

**Synthesis of the azidomethyl-functionalized alkoxyamine:**

15

According to the protocol from C.J. Haker, *et al.*, (*J. Polym. Sci. Part A: Pol. Chem.*

**1998, 36, 2161-2167**), a 100 mL ovendried Schlenk-flask equipped with a magnetic stirring bar and a rubber septum was charged under argon atmosphere with the chloromethyl functionalized alkoxyamine (**19e**) (2.00 g, 5.34 mmol) and sodium azide ( $\text{NaN}_3$ ) (694 mg, 10.68 mmol). The reactants were dissolved in 20 mL of anhydrous dimethylformamide

20

(DMF) and heated under an atmosphere of argon to  $50^\circ\text{C}$  for 3 h. The reaction course was monitored by t.l.c. After complete consumption of the starting material, the reaction mixture was quenched with 100 mL of water. The aqueous phase was diluted with diethyl ether (50 mL) and was then extracted with diethyl ether (3 x 50 mL). The combined organic extracts were successively washed with water (50 mL) and brine (50 mL) and dried over  $\text{MgSO}_4$ .

superimposed, 2H,  $CH_2NH_2$ ), 3.66 (s, superimposed, 2H,  $CH_2NH_2$ ), 3.53 (d,  $J = 10.5$  Hz, 1H, NCH), 3.45 (d,  $J = 10.8$  Hz, 1H, NCH), 2.63-2.47 (br. m, 1H,  $CH(CH_3)_2$ ), 1.72 (d,  $J = 6.6$  Hz, 3H,  $CH(CH_3)_2$ ), 1.65 (d,  $J = 6.6$  Hz,  $CH(CH_3)_2$ ), 1.62-1.50 (br. m, superimposed, H,  $CH(CH_3)_2$ ), 1.51 (d,  $J = 6.3$  Hz, 3H,  $CHCH_3$ ), 1.21 (s, 9H,  $C(CH_3)_3$ ), 1.15 (d,  $J = 5.1$  Hz, 3H, 5  $CHCH_3$ ), 0.99 (s, 9H,  $C(CH_3)_3$ ), 0.76 (d,  $J = 6.6$  Hz,  $CH(CH_3)_2$ ), 0.45 (d,  $J = 6.3$  Hz,  $CH(CH_3)_2$ ) ppm.  $^{13}C$  NMR (75 MHz,  $d^6$ -benzene, room temp., both diastereoisomers):  $\delta$  144.24, 143.51, 142.74, 142.68, 142.62, 131.27, 131.23; 127.85, 127.24, 127.14, 126.85, 126.68, 126.43, 83.93, 83.07, 72.71, 60.68, 60.61, 46.45, 32.38, 32.09, 28.64, 28.50, 24.91, 23.48, 22.56, 22.24, 21.40, 21.39 ppm.

10

**PART K****Synthesis of the hydroxy-functionalized alkoxyamine:**

The following Scheme 11 was followed in this part.

15

**Scheme 11:**

(25) was added dropwise with a syringe. The reaction mixture was stirred at room temp. for two hours and the reaction course was monitored by t.l.c. After complete conversion, dichloromethane was evaporated under reduced pressure, the residue was dissolved in EtOAc (200 mL) and 100 mL of an aqueous 5 % KHSO<sub>4</sub>-solution were added. After phase separation, the aqueous phase was extracted with EtOAc (2 x 100 mL) and the combined organic extracts were washed successively with aqueous 5 % KHSO<sub>4</sub>-solution (2 x 100 mL), saturated aqueous NaHCO<sub>3</sub>-solution (100 mL), water (100 mL) and brine (100 mL). The solution was dried over MgSO<sub>4</sub>, filtered off and the solvent was evaporated under reduced pressure to yield ca. 9.6 g (> 95 %) of the benzamide as a colorless solid of sufficient purity for the next step according to NMR, GC/MS and t.l.c. analysis. *R*<sub>f</sub>: 0.24 (EtOAc/hexanes = 1:1, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.): δ 7.71-7.67 (m, 2H, Ar-H), 7.49-7.35 (m, 3H, Ar-H), 6.29 (s, 1H, NH), 4.82 (t, *J* = 6.0, 1H, OH), 3.64 (d, *J* = 6.0, 2H, CH<sub>2</sub>), 1.38 (s, 6H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp.): δ 168.37, 134.80, 131.53, 128.52, 126.85, 70.63, 56.34, 24.56 ppm.

15 A 1000 mL ovendried Schlenk-flask equipped with a magnetic stir bar and rubber septum was charged under an atmosphere of argon with ca. 9.6 g (50.0 mmol) of the benzamide. The compound was dissolved in 250 mL of anhydrous diethylether. After cooling to 0 °C (icebath), a 1.0 M solution of LiAlH<sub>4</sub> in diethylether (100 mL) was added dropwise with a syringe. The reaction mixture was stirred with warming to room temp. for 24 hours and then heated to reflux for additional four hours. The reaction course was monitored by t.l.c. After complete conversion, the reaction was quenched by successive addition of 4.2 mL of water, 4.2 mL of an aqueous 5 % NaOH-solution, followed by additional 4.2 mL of water. The colorless precipitate is filtered off by a glass-sintered funnel and the filtercake was washed thoroughly with diethylether. The combined organic filtrates were evaporated under reduced pressure to yield 7.90 g (88 %, 2 steps) of pure amine 26 as a colorless solid. *R*<sub>f</sub>: 0.31 (EtOAc/hexanes = 2:1 + 2% NEt<sub>3</sub>, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.): δ 7.60-7.20 (m, 5H, Ar-H), 4.69 (s, 1H, OH), 3.72 (s, 2H, CH<sub>2</sub>OH), 3.38 (s, 2H, CH<sub>2</sub>N), 2.27 (br. s, 1H, NH), 1.20 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp.): δ 140.74, 128.43, 128.31, 128.15, 127.23, 126.97, 68.35, 53.92, 46.40, 24.13 ppm.

reduced pressure. Purification by MPLC (silica gel, EtOAc to yield ca. 9.6 g (> 95 %) of the benzamide as a colorless solid of sufficient purity for the next step.  $R_f$ : 0.34 (EtOAc/hexanes = 1:4, UV<sub>254</sub>-quenching). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  8.29-8.20 (m, 2H, Ar-H), 7.50 (s, 1H, CH(=N)), 7.44-7.31 (m, 3H, Ar-H), 3.79 (s, 2H, CH<sub>2</sub>OH), 1.53 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 0.81 (s, 9H, SiC(CH<sub>3</sub>)<sub>3</sub>), -0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, room temp.):  $\delta$  132.01, 131.00, 129.94, 128.82, 128.30, 74.12, 68.25, 25.70, 23.03, 18.09, -5.60 ppm.

### K.3: Synthesis of the nitroxide 29:

According to a protocol of R. Braslau, C.J. Hawker, et al. (*J. Am. Chem. Soc.* 1999, 121, 3904-3921) and the general synthetic protocol described for the synthesis of alkoxyamines 19, in an ovendried 100 mL Schlenk-flask equipped with a magnetic stir bar and a rubber septum were placed 3.488 g (11.4 mmol) of the protected nitrone 28. The chemical was dissolved in 40 mL of anhydrous tetrahydrofuran (THF) and the solution was cooled to 0 °C (icebath). 11.4 mL of a 2 M solution of isopropylmagnesium chloride (4) were added dropwise at this temperature and stirring was continued with warming to room temp. for 12 hours. The reaction mixture was quenched with a saturated aqueous NH<sub>4</sub>Cl-solution (20 mL) and the THF was evaporated under reduced pressure. The reaction mix was diluted with diethyl ether (100 mL) and water (30 mL). After phase separation, the aqueous phase was extracted with diethyl ether (2 x 50 mL) and the combined organic extracts were washed successively with water (50 mL) and brine (50 mL), dried over MgSO<sub>4</sub>, filtered and evaporated under reduced pressure to yield ca. 3.3 g (82 %) of the crude hydroxylamine as an orange oil which was used directly without further purification in the next step. The crude material contained some of the corresponding nitroxide due to air oxidation during the work-up procedure.  $R_f$ : 0.65 (EtOAc/hexanes = 1:9, UV<sub>254</sub>-quenching).

According to a protocol of R. Braslau, C.J. Hawker, et al. (*J. Am. Chem. Soc.* 1999, 121, 3904-3921), and the general synthetic protocol described for the synthesis of alkoxyamines 19, 3.3 g (9.4 mmol) of the crude intermediate hydroxylamine, dissolved in a mixture of MeOH (50 mL) and 28 % aqueous NH<sub>4</sub>OH-solution (10 mL) were air-oxidized in the presence of 85 mg (0.47 mmol) of Cu(OAc)<sub>2</sub> to yield the crude nitroxide as a dark red

105 - 110°C until the evolution of nitrogen ceased. Xylene was evaporated in vacuo and 1 mL of petroleum ether was added to the reaction mixture to yield an orange solution. 5 mL of MeOH were added under vigorous stirring and after phase separation and removal of the supernatant, the methanolic layer was partially concentrated and placed in a refrigerator at 5 approximately -20°C causing colorless crystals to form. Excess MeOH was removed and the residue was dissolved in approximately 2 mL of MeOH under gentle heating. The solution was again cooled to approximately -20°C and, after collection, the crystals were dried in vacuo to yield 401 mg (27 %) of the desired compound. TLC (1:9 EtOAc/hexanes):  $R_f = 0.60$ ;  $^1\text{H}$  NMR (300 MHZ,  $\text{CDCl}_3$ ):  $\delta = 1.22$  (s, 3H,  $\text{CH}_3$ ), 1.34 (s, 3H,  $\text{CH}_3$ ), 1.37 (s, 3H,  $\text{CH}_3$ ), 1.43 (s, 3H,  $\text{CH}_3$ ), 1.4-1.7 (m, superimposed, 3H,  $\text{CH}_2\text{CHHCH}$ ), 1.74 (s, 3H,  $\text{CH}_3$ ), 1.76 (s, 3H,  $\text{CH}_3$ ), 1.95 (dq,  $J = 12.0, 9.6$  Hz, 1H,  $\text{CH}_2\text{CHHCH}$ ), 3.30 (dd,  $J = 10.1, 5.9$  Hz, 1H,  $\text{CH}_2\text{CHHCH}$ ) ppm;  $^{13}\text{C}$  NMR (75 MHZ,  $\text{CDCl}_3$ ):  $\delta = 20.85, 21.60, 22.03, 24.96, 26.09, 28.44, 34.90, 37.31, 39.34, 66.37, 72.33, 73.86, 121.39, 126.01$  ppm.

15 **Example 3: Comparison: TEMPO in emulsion polymerization:**

Twelve (12) separate emulsion polymerization conditions were conducted with three different initiators, all at 90°C for 15 h (a total of 36 experiments). Each polymerization was set up with a total volume 0.7 mL, with 20 weight % styrene (monomer). The amount of surfactant (sodium alpha ( $\text{C}_{14}\text{-C}_{16}$ ) olefin sulfonate - sold by Rhodia as Rhodacal A-246/L) 20 added was 1 weight % to monomer, and the amount of initiator added was 0.001 mole equivalence to monomer. The initiators that were used were water soluble and were (1) potassium persulfate, (2) *tert*-butylhydroperoxide (TBHP) and (3) 2,2-azobis( $\text{N,N}'$ -dimethyleneisobutyramidine) dihydrochloride (sold by E. I. du Pont de Nemours and Company under the trademark VAZO® 044). For each initiator the series of 12 25 polymerizations differed in the amount of control agent added, with the first well getting no control agent and the last well getting 3.3 mole equivalence of control agent, with even steps of 0.3 mole equivalence (the control agent used was 2,2,6,6-tetramethyl-1-piperidinoxyl radical - "TEMPO"). After the predetermined heating and agitation time and temperature the polymerization mixtures were worked up and characterized using the standard procedure 30 outlined for polymerization experiments at the beginning of the Example section.

( $M_w$ ) and the conversions are reduced in an almost linear fashion. Table 7, below provides selected molecular weight and conversion data.

Table 7:

Initiator	$\alpha$ -hydrido-nitroxide to initiator ratio	$M_w$	Conversion
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0:1	749,265	99
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.3:1	527,763	98
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.6:1	326,648	69
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.9:1	146,769	26
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1.2:1	102,554	10
TBHP	0:1	544,236	97
TBHP	0.3:1	541,576	80
TBHP	0.6:1	155,490	44
TBHP	0.9:1	143,790	60
TBHP	1.2:1	77,163	46
TBHP	1.5:1	19,000	13
VAZO®044	0:1	570,640	95
VAZO®044	0.3:1	252,908	44
VAZO®044	0.6:1	111,664	26

5

Example 5:

Sixty four stable free radical polymerization (SFRP) were carried out under aqueous emulsion conditions. Each polymerization was set up with a total volume 0.7 mL, with 20 weight % styrene (monomer). The amount of surfactant (sodium alpha (C<sub>14</sub>-C<sub>16</sub>) olefin sulfonate - sold by Rhodia as Rhodacal A-246/L) added was 1 weight % to monomer, and four different amounts of initiator were added: 0.001, 0.002, 0.003 and 0.004 mole equivalence to monomer. The two initiators that were used were water-soluble and were (1) potassium persulfate, (2) *tert*-butylhydroperoxide (TBHP). For each initiator the series of seven polymerizations differed in the amount of control agent added, with the first well getting 0.6 mole equivalence control agent and the last well getting 1.2 mole equivalence of control agent, with even steps of 0.1 mole equivalence (the control agent used was 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide – “ $\alpha$ -hydrido-nitroxide”). In addition a polymerization reaction without control agent was conducted for each initiator type and amount. Four chemically identical copies were made, agitated and heated at 90°C for 3, 7, 15 and 30 h respectively (thus a total of 256 different polymerizations were actually carried out).

monomer. The initiator that was used was water soluble and was *tert*-butylhydroperoxide (TBHP). For each initiator concentration the series of seven polymerizations differed in the amount of control agent added, with the first well getting 0.6 mole equivalence control agent and the last well getting 1.2 mole equivalence of control agent, with even steps of 0.1 mole equivalence (the control agent used was 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide - "α-hydrido-nitroxide"). In addition a polymerization reaction without control agent was conducted for each amount of initiator. After the predetermined heating and agitation time of 90 °C and 30 h the reactor vessels were opened and a small aliquot was taken from each vessel for analysis. Subsequently, an amount of *n*-butylacrylate equal to the amount of styrene previously added (10 wt %) was dispensed to each vessel. The vessels were then resealed and heated at 90°C and mixed for an additional 30 h. Subsequently the reaction mixtures were worked up and characterized using the standard procedure outlined for polymerization experiments at the beginning of the Example section.

Figure 4 is a bar graph of the molecular weight versus the amounts of control agent for both steps of the block copolymerization. After the second stage of polymerization, there was a clear increase of the molecular weights as compared to the molecular weights obtained after polymerization of just the first monomer, suggesting block copolymer formation. In addition, the overall molecular weights still depended on the ratio of 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (α-hydrido-nitroxide control agent) to initiator which suggests that the polymerization had not lost its living character.

#### Example 7: Block *n*-Butylmethacrylate/Styrene Polymers

Twenty four stable free radical polymerization (SFRP) were carried out under aqueous emulsion conditions. Each polymerization was set up with a total volume 0.7 mL, with 10 weight % *n*-butylmethacrylate (monomer). The amount of surfactant (sodium alpha (C<sub>14</sub>-C<sub>16</sub>) olefin sulfonate - sold by Rhodia as Rhodacal A-246/L) added was 1 weight % to monomer, and three different amounts of initiator were added: 0.001, 0.002 and 0.003 mole equivalence to monomer. The initiator that was used was water soluble and was *tert*-butylhydroperoxide (TBHP). For each initiator concentration the series of seven polymerizations differed in the amount of control agent added, with the first well getting 0.6 mole equivalence control agent and the last well getting 1.2 mole equivalence of control

Initiator Concentration	$\alpha$ -hydrido-nitroxide to initiator ratio	$M_w$ of n-butyl- methacrylate	$M_w$ of block copolymer
0.003	0.8:1	69,326	241,970
0.003	0.9:1	54,997	125,490
0.003	1:1	49,282	192,670
0.003	1.1:1	32,574	Er
0.003	1.2:1	20,079	Er
0.003	0:1	2,768,000	--

In Table 8, "Er" indicates an error in the testing and "—" indicates no data was taken.

**Example 8: Stepwise Addition of Monomers**

5 Sixteen stable free radical polymerization (SFRP) were carried out under aqueous emulsion conditions. Each polymerization was designed to have the following final conditions for the growth of the first block: total volume of 0.7 mL, with 10 weight % of monomer, one weight % to monomer of surfactant (sodium alpha ( $C_{14}$ - $C_{16}$ ) olefin sulfonate - sold by Rhodia as Rhodacal A-246/L), and two different amounts of initiator (0.001, 0.002 mole equivalence to monomer). The initiator used was an adduct of the initiator/control agent (the organic soluble 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane) (eight identical reactions were run at each initiator to monomer ratio). This compound predetermines the control agent to initiator ratio to equal one. The reaction was split into two stages, with all the components except monomer being added in the first step. In the first step 10 25 % of the total monomer (2.5 wt %) was added as styrene, the plate was then sealed and heated at 90°C for 6 h. The reactor vessels was then allowed to cool, opened and 75 % of the total monomer (7.5 weight %) of styrene was added to each reaction vessel. The vessel was then resealed and heated at 90 °C for an additional 30 h. After the predetermined heating and agitation time the reactor vessels were cooled to room temperature and opened and a small 15 aliquot was taken from each vessel for analysis.

15 20

Subsequently, an amount of *n*-butylacrylate equal to the amount of styrene previously added (10 wt %) was dispensed to each vessel. The vessels were then resealed and heated at 90°C and mixed for an additional 30 h. Finally, the reaction mixtures were worked up and characterized using the standard procedure outlined for polymerization experiments at the 25 beginning of the Example section.

n-butylacrylate added in the reinitiation step. Table 9 below provides selected weight average molecular weights for the styrene polymer and the block copolymer.

Table 9:

Wt % styrene	Wt % n-butyl-acrylate	Initiator Concentration	M <sub>w</sub> of styrene block	M <sub>w</sub> of block copolymer
10	5	0.0005	75,000	165,000
10	10	0.0005	75,000	234,000
10	15	0.0005	75,000	238,000
10	20	0.0005	75,000	248,000
10	25	0.0005	75,000	277,000
10	30	0.0005	75,000	300,000
10	5	0.001	48,000	125,000
10	10	0.001	48,000	127,000
10	15	0.001	48,000	143,000
10	20	0.001	48,000	145,000
10	25	0.001	48,000	150,000
10	30	0.001	48,000	155,000
10	5	0.002	20,000	49,000
10	10	0.002	20,000	52,000
10	15	0.002	20,000	55,000
10	20	0.002	20,000	59,000
10	25	0.002	20,000	62,000
10	30	0.002	20,000	69,000
10	5	0.003	17,000	35,000
10	10	0.003	17,000	37,000
10	15	0.003	17,000	39,000
10	20	0.003	17,000	44,000
10	25	0.003	17,000	51,000
10	30	0.003	17,000	66,000
5	5	0.0005	70,000	156,000
5	10	0.0005	70,000	183,000
5	15	0.0005	70,000	248,000
5	20	0.0005	70,000	412,000
5	25	0.0005	70,000	433,000
5	30	0.0005	70,000	--
5	5	0.001	50,000	100,000
5	10	0.001	50,000	105,000
5	15	0.001	50,000	110,000
5	20	0.001	50,000	--
5	25	0.001	50,000	--
5	30	0.001	50,000	197,000
5	5	0.002	19,000	--

FIG. 8 is a bar graph illustrating the reinitiation of Mw 75,000 styrene blocks in the presence of acrylic acid. The molecular weight increase seen in the presence of larger amounts of acrylic acid is believed to be due to continued styrene polymerization with incorporation of acrylic acid. Table 10 below provides selected weight average molecular weights for the styrene polymer and the block copolymer.

Table 10:

Wt % styrene	Wt % acrylic acid	Initiator Concentration	M <sub>w</sub> of styrene block	M <sub>w</sub> of block copolymer
10	0	0.0005	71,000	71,000
10	1	0.0005	71,000	95,000
10	2	0.0005	71,000	112,000
10	5	0.0005	71,000	125,000
10	7.5	0.0005	71,000	147,000
10	10	0.0005	71,000	--
10	0	0.001	51,000	51,000
10	1	0.001	51,000	62,000
10	2	0.001	51,000	64,000
10	5	0.001	51,000	83,000
10	7.5	0.001	51,000	--
10	10	0.001	51,000	--
10	0	0.002	25,000	25,000
10	1	0.002	25,000	27,000
10	2	0.002	25,000	28,000
10	5	0.002	25,000	29,000
10	7.5	0.002	25,000	30,000
10	10	0.002	25,000	32,000
10	0	0.003	19,000	19,000
10	1	0.003	19,000	20,000
10	2	0.003	19,000	20,000
10	5	0.003	19,000	21,000
10	7.5	0.003	19,000	--
10	10	0.003	19,000	25,000
5	0	0.0005	78,000	78,000
5	1	0.0005	78,000	86,000
5	2	0.0005	78,000	--
5	5	0.0005	78,000	--
5	7.5	0.0005	78,000	138,000
5	10	0.0005	78,000	--
5	0	0.001	37,000	37,000
5	1	0.001	37,000	42,000
5	2	0.001	37,000	--

30 hours. The reaction mixtures were worked up and characterized using the standard procedure outlined for polymerization experiments at the beginning of the Example section.

FIG. 9 is a bar graph illustrating the relationship between the overall molecular weight of the random copolymer and the amount of acrylic acid added to the emulsion 5 polymerization. Table 11.

**Table 11:**

Initiator Concentration	Wt % acrylic acid	M <sub>w</sub> of styrene/acrylic acid	M <sub>w</sub> of block copolymer
0.003	0	4800	23,000
0.003	1	5000	24,000
0.003	2	10,000	26,000
0.003	5	17,000	31,000
0.003	7.5	22,000	35,000

**Example 12: Cyclic nitroxide adducts**

10 Four stable free radical polymerization reactions were carried out under aqueous emulsion conditions. Each polymerization was set up to have the following final conditions for the growth of a first polymer block: total volume 0.7 mL, with 10 weight % of styrene (monomer). The amount of surfactant (sodium alpha (C<sub>14</sub>-C<sub>16</sub>) olefin sulfonate - sold by Rhodia as Rhodacal A-246/L) added was 1 weight % to monomer, and two different amounts 15 of initiator were added: 0.001 or 0.002 mole equivalents to monomer. The initiator used was an adduct of the initiator/control agent (5,5-dimethyl-(1-pyrroline-N-oxide/AIBN adduct). This compound predetermines the control agent to initiator ratio to equal one. Four identical reactions were run at each initiator to monomer ratio.

20 A block was assembled in two stages, with all the components except monomer being added in the first step. In the first step 2.5 wt % of styrene (25 % of the total first monomer) was added to each reaction vessel, and the plate was sealed and heated at 90°C for 2 hours. The reactor vessels were allowed to cool, opened and the remaining 7.5 wt % of styrene (75 % of the first monomer) was added to each reaction vessel. The plate was resealed and heated at 90°C for an additional 30 hours. After the predetermined heating and agitation time 25 the reactor vessels were cooled to room temperature and opened and a small aliquot was taken from each vessel for analysis.

Subsequently, 10 wt % of a second monomer, *n*-butylacrylate, was dispensed to half of the vessels. The vessels were then resealed and heated at 90°C and mixed for an additional 30 hours. The reaction mixtures were worked up and characterized using the standard

**Example 14: Polymer Characterization****A. Particle Size Determination**

5      Particle sizes were determined using dynamic light scattering measurements performed at a temperature of 308K in nanopure H<sub>2</sub>O on diluted latex samples, at a scattering angle of 90 degrees and a laser wavelength of 800 nm (Precision Detectors). The intensity-intensity autocorrelation function was analyzed using a second order cumulant analysis. A sample plot is illustrated in FIG. 10. In this example, the average hydrodynamic  
10     radius was 29 nm (first order cumulant) and the polydispersity index was smaller than 0.09 (second order cumulant), indicating an essentially monodisperse latex.

**B. Small Angle X-Ray Scattering**

15     Small angle X-ray scattering (SAXS) measurements were conducted using a custom laboratory source consisting of a rotating anode X-ray generator with a copper target equipped with a nickel foil filter and dual Franks mirrors for monochromatization and focussing of the beam. Films were mounted in copper blocks inside an evacuated sample chamber and annealed at 120°C for five minutes prior to measurement at that temperature. Scattering images were recorded over 300 s by a two-dimensional multiwire area detector and reduced to a one-dimensional profile by integrating azimuthally along an arc located  
20     ±30° from the direction normal to the sections composing the specimen. Data were reported in the form of total counts as a function of q, the scattering momentum transfer, defined as  $4\pi/\lambda \sin \theta$ , where  $\lambda = 1.54 \text{ \AA}$  is the wavelength of the radiation and  $\theta$  is the angle between the transmitted and the scattered radiation.

25     Films for scattering measurements were prepared by dissolution of sufficient polymer in toluene to yield an approximate concentration of 5 wt%. The resulting solution was placed on top of a water column and the solvent was permitted to evaporate at room temperature and atmospheric pressure over 48 hours. Use of water as a casting substrate minimizes the mechanical deformation of the film upon removal from the casting vessel. The resulting polymer film was removed from the water column and dried first in air for at least 2 hours,  
30     and then in vacuum at room temperature for at least 2 hours. The film was cut into sections approximately 3 x 5 mm in area, and between 3 and 5 sections were stacked to yield a specimen between 1 and 2 mm in thickness. Stacked specimens were then placed in an evacuated oven and annealed for at least 48 hours at 120°C to remove any residual solvent.

35     FIG. 11 illustrates the results of SAXS of a polystyrene-block-poly(butyl acrylate) copolymer prepared according to Example 11, above (10 wt % styrene, 10 wt % butyl acrylate, 0.001 equivalents initiator). One scattering maximum is observed, at a position

prepared in identical manner, to allow for different staining procedures). The specimens were then annealed in a vacuum oven for approximately 18 hours at 125°C. In order to provide contrast between the domains in the electron microscope, the samples were stained with RuO<sub>4</sub> vapors (RuO<sub>4</sub> staining kit from SPI Supplies, part # 02592-AB ). An aqueous 5 RuO<sub>4</sub> solution was prepared following the supplier's instructions. The specimen grids and an open vial containing the RuO<sub>4</sub> solution were placed underneath an inverted crystallizing dish, so that the specimens would be exposed to an atmosphere saturated with RuO<sub>4</sub> vapors. Individual specimens were removed at times of 5, 15, 30, and 60 minutes, in order to 10 optimize the exposure time for maximum contrast. It was found that exposure times of 30 and 60 minutes gave the best results.

FIGS. 13A and 13B are reproduced from a negative which was captured at a magnification of 30,000 from a styrene-butyl acrylate polymer film prepared according to Example 11, above (10 wt % styrene, 10 wt % butyl acrylate, 0.001 equivalents initiator). The images show a region at the boundary between two sections of film having different 15 thickness. The film thickness is restricted to a set of discrete values, as discussed above. At the boundary between these sections, a fairly regular microstructure is clearly observed. The period of the microstructure is obtained by dividing the period on the negative by the magnification, which gives approximately  $1.1 \text{ mm}/30,000 = 36 \text{ nm}$ . The type of morphology shown in FIGS. 13A and 13B is essentially identical to that reported in B. L. Carvalho and 20 E.L Thomas, *Phys. Rev. Lett.*, 73, pp 3321-4, for a styrene-block-isoprene copolymer with a lamellar morphology and a molecular weight of 108,000 gm/mol, using a similar sample preparation method. In both cases, the lamellae in most parts of the film lie parallel to the carbon film in most parts of the image, and are thus not visible. However the lamellae are 25 oriented vertically at the boundaries between regions containing different number of layers, as this configuration has a lower free energy than other types of defects which could occur at such a boundary.

#### Example 15: Preparation of Seed Emulsions

A. Copolymer of styrene:*t*-butylacrylamide:2-acrylamido-2-methylpropanesulfonic acid (AMPS) 1:1:0.02 by weight.  
30 In a 250 mL Morton flask (fitted with mechanical stirrer, thermometer, and oil bath heating) under argon atmosphere were combined 2-acrylamido-2-methylpropanesulfonic acid

(0.10g), *t*-butylacrylamide (Aldrich, 9.9g),  $\alpha$ -olefin sulfonate surfactant (Rhodia, Rhodacal A-246/L, 12.5 g of a ca. 40% aqueous solution), and water (175 g). The mixture was stirred and heated in a 90° C oil bath until an internal temperature of ca. 75° C was obtained, and then solid initiator ( $K_2S_2O_8$ , Aldrich, 0.20 g) was added all at once. The appearance of the  
5 aqueous monomer slurry changed quickly over a period of 1-4 minutes, with the solid dissolving to form a nearly transparent, bluish scattering emulsion. The mixture was stirred and heated in a 100° C oil bath for an additional 2 h (internal temperature of 93° C) to decompose the excess initiator. The mixture was cooled with stirring, and filtered to remove any suspended solid. Yield 196.2 g of emulsion, pH ca. 3 to pH paper, 8.07 % solids, particle  
10 size = 9.3 nm  $R_h$ , by DLS, (2nd cumulant analysis PDI = 0.10).

**D. Copolymer of butyl acrylate:4-styrenesulfonic acid sodium salt 1:0.01 by weight.**

In a 250 mL Morton flask (fitted with mechanical stirrer, thermometer, and oil bath heating) under argon atmosphere were combined 4-styrenesulfonic acid sodium salt hydrate (0.20g), butyl acrylate (Aldrich, 20.0 g),  $\alpha$ -olefin sulfonate surfactant (Rhodia, Rhodacal A-246/L, 25.0 g of a ca. 40% aqueous solution), and water (145 g). The mixture was stirred and heated in a 90° C oil bath until an internal temperature of ca. 75° C was obtained, and then a  
15 solution of initiator ( $K_2S_2O_8$ , Aldrich, 0.40 g, dissolved in 10 mL  $H_2O$ ) was added all at once  
20 via a syringe. The appearance of the nearly opaque aqueous monomer emulsion changed quickly over less than 5 minutes to form a translucent, bluish scattering emulsion. The mixture was stirred and heated for an additional 6 h in the 90° C oil bath to decompose the excess initiator. The mixture was cooled with stirring, and filtered to remove a small amount  
25 of suspended solid. Yield 197.5 g of emulsion, pH ca. 3.5 to pH paper, 15.75% solids, particle size = 14.7 nm  $R_h$ , by DLS, (2nd cumulant analysis PDI = 0.18).

**E. Copolymer of styrene:4-styrenesulfonic acid sodium salt 1:0.01 by weight.**

In a 250 mL Morton flask (fitted with mechanical stirrer, thermometer, and oil bath heating) under argon atmosphere were combined 4-styrenesulfonic acid sodium salt hydrate (0.20g), butyl acrylate (Aldrich, 20.0 g),  $\alpha$ -olefin sulfonate surfactant (Rhodia, Rhodacal A-246/L, 25.0 g of a ca. 40% aqueous solution), and water (145 g). The mixture was stirred and  
30

turbid over a period of ca. 30 minutes, with shaking repeated ever few minutes. The loaded seed was allowed to stand at ambient temperature for ca. 3 days with no apparent visual change. The mixture was uncapped and heated in a 100° C oil bath with magnetic stirring for 2 minutes, and then stirred uncapped at ambient temperature in a fume hood for 30 minutes,  
5 to allow most of the CH<sub>2</sub>Cl<sub>2</sub> to evaporate. Then 250 µL of styrene was added, the mixture was capped and stirred for 1 hour, until the styrene appeared to load, resulting in a translucent dispersion visually similar to the starting seed emulsion, with a small amount of suspended solid. The mixture was filtered through a small glass-fiber mat to remove the solid. The pH was measured with pH paper as ca. 8.

10

### B. Living Emulsion Polymerization of Styrene

The loaded seed emulsion from procedure A in this example was added to a stirred 250 mL Morton flask (equipped with magnetic stirrer, thermometer, under argon atmosphere)  
15 containing degassed water (150 mL). The pH was ca. 7 to pH paper. Then 1.8 mL of a 10% by weight solution of AMPS monomer (2-acrylamido-2-methylpropane sulfonic acid) in water was added, and the pH was found to be ca. 3.5 to pH paper. The flask was placed into an oil bath heated to 100° C, which maintained an internal temperature of ca. 93° C. After 40 minutes, a 1 mL sample (Sample 16-1) of the emulsion was withdrawn for analysis, and then  
20 2 mL degassed styrene was added. A 1 mL sample (Sample 16-2) was withdrawn for analysis after 5 h total reaction time, and 10 mL additional degassed styrene monomer was added. A 1 mL sample (Sample 16-3) was withdrawn for analysis after 16 h total reaction time, and 10 mL additional degassed styrene monomer was added, completing the addition of 20g of total styrene planned (aiming for 20 g monomer/180 g total emulsion). A 1 mL  
25 sample (Sample 16-4) was withdrawn for analysis after 22.3 h total reaction time. After 40.7 h total reaction, another sample (Sample 16-5) was removed, and the reaction mixture was cooled with stirring, the resulting white-translucent emulsion was filtered to remove suspended solid (ca. 1.5 g of solid styrene coagulum was isolated). Yield 170.3g emulsion, 10.31% solids, 0.90% total residual styrene (by quantitative GC analysis, 8.1% of total  
30 styrene added, corresponding to 91.9% monomer conversion to polymer). Molecular weight by traditional GPC (THF eluent) showed a peak molecular weight of 89,400, M<sub>n</sub> of 70,400,

Analysis of the emulsion showed 13.5% solids, Mp by GPC (THF eluent) of 133,000, Mw = 158,300, Mn = 96,100, Mw/Mn = 1.65. Particle size by DLS was found to be  $R_h = 41.4$  nm, 2nd cumulant analysis PDI = 0.04. The molecular weight increase and particle size increase are consistent with chain extension of the living chains in the emulsion with additional 5 styrene. Overlay of the GPC traces before and after the chain extension procedure suggests that essentially the entire molecular weight distribution shifted to higher molecular weight.

#### D. Chain Extension of the Living Styrene Emulsion with Butyl Methacrylate Monomer

10 In a 50 mL capacity 3-neck round-bottom flask, equipped with a magnetic stirbar, thermometer, and nitrogen inlet was placed 30.0 mL of the emulsion prepared in procedure B in this example, above, followed by 3.5 mL degassed butyl methacrylate. The flask was heated in a 95° C oil bath with stirring for 6 days, with daily sampling of ca. 0.5 mL aliquots for analysis. Percent solids and molecular weight increased for about 30 hours. After 30 15 hours, the percent solids decreased as coagulum formed, while molecular weight continued to increase for an additional 24 hours. The mixture was cooled and the emulsion was decanted from a significant amount of coagulum. Analysis of the emulsion showed 9.80% solids, Mp by GPC of 124,900, Mw = 161,400, Mn = 95,400, Mw/Mn = 1.7. Particle size by DLS was measured as  $R_h = 40.4$  nm.  $^1H$  NMR analysis of a dried sample of the polymer from the 20 emulsion in  $CDCl_3$  showed a broad peak at 3.9 ppm, consistent with the methylene signals of the butyl ester incorporated in the polymer. Comparison of the integrals of the ester peak with the aromatic polystyrene peaks indicated the presence of 21 weight percent of butyl methacrylate. Overlay of the GPC traces before and after the chain extension procedure indicate that essentially the entire molecular weight distribution shifted to higher molecular 25 weight.

#### E. Chain Extension of the Living Styrene Emulsion with Methyl Methacrylate / 2-(2-Oxo-1-imidazolidinyl)ethyl Methacrylate Monomer Mixture

In a 10 mL capacity round-bottom flask, equipped with a magnetic stirbar, in a 30 nitrogen-filled glovebox was placed 9.0 mL of the emulsion prepared in procedure B, in this example, above, followed by 0.9 mL a commercially available 25 wt.% solution of 2-(2-oxo-

become less turbid over a period of ca. 15 minutes, with shaking repeated every few minutes for 30 minutes. The mixture was uncapped and heated in a 100° C oil bath with magnetic stirring for 2 minutes, and then stirred uncapped at ambient temperature in a fume hood for 30 minutes, to allow most of the CH<sub>2</sub>Cl<sub>2</sub> to evaporate. Then 250 µL of styrene was added,  
5 the mixture was capped and stirred for 30 minutes, until the styrene appeared to load, resulting in a translucent dispersion visually similar to the starting seed emulsion, with a small amount of suspended solid. The mixture was filtered through a small glass-fiber mat to remove the solid.

10      **B. Living Emulsion Polymerization of Styrene**

The loaded seed emulsion from procedure A of this example was added to a stirred 250 mL Morton flask (equipped with magnetic stirrer, thermometer, under argon atmosphere) containing degassed water (160 mL). The bluish scattering, nearly transparent mixture was  
15 heated placed in a 100° C oil bath and heated to an internal temperature of 92° C for 0.5 hour. An aliquot of ca. 1 mL volume was removed for analysis (Sample 17-1), and a syringe pump was used to begin feed of 2.75 mL degassed styrene monomer over 2 hours, with the beginning of this feed marking the start of the polymerization process. After 2 hours, 2.9 mL  
20 of a 10% by weight of AMPS monomer in water was added, which lowered the pH of the polymerizing mixture from ca. 9 to ca. 3, and then the syringe pump was used to begin an 8 hour feed of 30 mL degassed styrene monomer. An additional nine sample aliquots (17-2 through 17-10) were withdrawn during the 8 hour feed and the remaining time of the 47 hour period during which the reaction was heated and stirred. A visible crust of coagulated or dried polymer had formed on the surface of the reaction mixture. The mixture was cooled  
25 with stirring, the coagulum was removed, and the emulsion was analysed. Yield of about 172 g of bluish scattering emulsion, 9.41% solids, particle size by DLS = 39.1 nm Rh, GPC (THF eluent) Mp = 66,800, Mw = 67,900, Mn = 26,700, with a noticeable peak at higher molecular weight corresponding to the seed polymer.

A summary of analyses of the reaction aliquots and final emulsion are contained in  
30 Table 15. The % solids were measured by weighing samples imbibed into glass fiber pads, with microwave drying. The % conversion from % solids is calculated by subtracting the

5% aqueous solution of the same surfactant present in the seed emulsion, (Rhodacal A-246/L, Rhodia), followed by similar shaking. A ninth vial was similarly prepared with 0.300 g of the nitroxide, and 5.00g of the butyl acrylate:styrenesulfonate seed emulsion described in Example 15D. The samples were briefly shaken about every 15 minutes for 3 hours, and then 5 were allowed to stand for three days. Visual observation of turbidity and color was noted during the entire procedure, using room light and a handheld red laser source to visualize scattering from large and small particles, and selected samples were examined by dynamic light scattering after standing for the three day period.

10 Table 16:

sample # /Seed used *	Type and g of seed added	g of 5% A246/L soln	Control or not	Visual @ 3h	Visual @ 3 days	3-day Particle R <sub>h</sub> by DLS	DLS 2nd cumulant PDI
18-1	15E / 20.0	0		loaded / orange	loaded / orange	14.6	.25
18-2	15E / 10.0	0		loaded / orange	loaded / orange	15.2	.28
18-3	15E / 5.0	0		loaded / orange	loaded / orange	18.1	.30
18-4	15E / 2.5	0		loaded / orange	loaded / orange	**	**
18-5	15E / 1.25	0		some creaming	unstable	**	**
18-6	0	20.0	Control	clear yellow	clear yellow	504.1	.64
18-7	0	5.0	Control	creaming orange	creaming orange	**	**
18-8	0	2.5	Control	creaming orange	creaming orange	**	**
18-9	15D / 5.0	0		loaded / orange	loaded / orange	25.4	.33

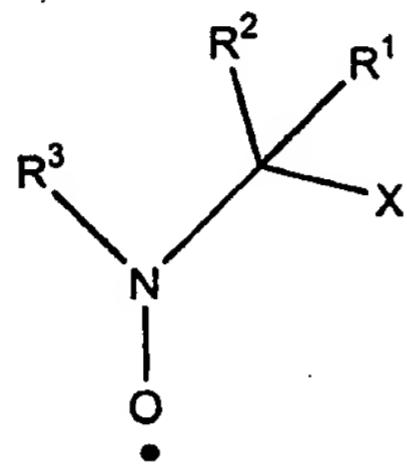
\* 0.30 g of nitroxide was added to each sample

\*\* indicates that the value was not measured for a particular sample

15 The most dilute control experiment, sample 18-6, appeared to be transparent yellow, perhaps with some of the nitroxide loading into the surfactant micelles. However, DLS showed the presence of very large particles in this system. The loaded seed emulsions of this example generally appeared to form small-particle loaded seed emulsions after 5-30 minutes. Particularly samples 1-4 and 9, are suitable for use in living emulsion polymerization processes with external free-radical initiator.

WHAT IS CLAIMED IS:

1        1. A method of forming a polymer emulsion comprising  
2                 combining water, at least one monomer, initiating radical, control agent and,  
3         optionally surfactant, to form a polymerization system, said control agent being characterized  
4         by the general formula:



5  
6        where X is a moiety that is capable of destabilizing said control agent on a  
7         polymerization time scale; and  
8                 each R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of alkyl,  
9         substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted  
10      heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy,  
11      silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally R<sup>1</sup> and R<sup>2</sup>  
12      are joined together in a ring structure; also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in a ring  
13      structure; and  
14                 forming a polymer from said at least one monomer.

1        2. The method of claim 1, wherein X is H.

1        3. The method of claim 1, wherein said R<sup>1</sup> is selected from the group consisting of  
2         alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, aryl, and substituted aryl.

1        4. The method of claim 3, wherein said R<sup>1</sup> is phenyl or pyridyl.

1        5. The method of claim 1, wherein said R<sup>2</sup> is selected from the group consisting of  
2         alkyl and substituted alkyl.

1        6. The method of claim 5, wherein said R<sup>2</sup> is isopropyl or methyl.

1        17. The method of claim 16, wherein said at least two different monomers are added  
2 to said polymerization system sequentially forming a block copolymer having at least two  
3 blocks.

1        18. The method of claim 17, wherein the weight average molecular weight of at least  
2 one block is greater than or equal to about 25,000.

1        19. The method of claim 16, wherein said at least two monomers are added to said  
2 polymerization system in a manner to form a random copolymer or higher order  
3 interpolymer.

1        20. The method of claim 1, further comprising controlling the molecular weight of  
2 said polymer.

1        21. The method of claim 20, wherein the weight average molecular weight of said  
2 polymer is greater than or equal to about 25,000.

1        22. The method of claim 1, further comprising controlling the particle size of said  
2 polymer.

1        23. The method of claim 22, wherein the hydrodynamic radius of said particle of said  
2 polymer is less than or equal to about 150 nanometers.

1        24. The method of claim 1, wherein said polymer is formed under polymerization  
2 conditions comprising living kinetics at a temperature of less than about 110°C.

1        25. The method of claim 1, further comprising re-initiating the propagation of said  
2 polymer by the addition of more monomer, which may be the same or different from any  
3 other previous monomer added to said polymerization system.

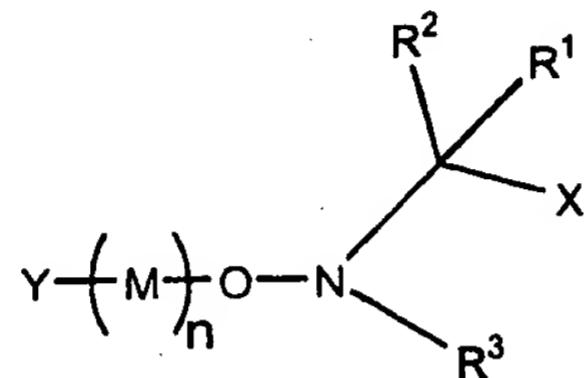
1        26. The method of claim 1, wherein said control agent is generated in said  
2 polymerization system in situ from a nitrone.

1        27. The method of claim 1, wherein said polymer has a polydispersity of less than  
2 about 2.0.

15 forming a polymer from said at least one monomer.

1        34. The method of claim 33, wherein Y is selected from the group consisting of  
2        fragments derived from a free radical initiator, alkyl, substituted alkyl, alkoxy, substituted  
3        alkoxy, aryl and substituted aryl.

1        35. A heterogeneous mixture comprising a plurality of particles, the particles  
2        comprising a compound characterized by the formula:



3        where X is a moiety that is capable of destabilizing said control agent on a  
4        polymerization time scale, Y is a moiety capable of initiating a free radical polymerization;  
5        each R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of alkyl,  
6        substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted  
7        heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy,  
8        silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally R<sup>1</sup> and R<sup>2</sup>  
9        are joined together in a ring structure; also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in a ring  
10      structure;

12      M is one or more monomers; and n is an integer greater than or equal to 0.

1        36. The mixture of claim 35, wherein X is hydrogen.

1        37. The mixture of claim 35, wherein M is selected from the group consisting of  
2        styrene, substituted styrene, alkyl acrylate, substituted alkyl acrylate, alkyl methacrylate,  
3        substituted alkyl methacrylate, acrylic acid, methacrylic acid, acrylonitrile, methacrylonitrile,  
4        acrylamide, methacrylamide, N-alkylacrylamide, N-alkylmethacrylamide, N,N-  
5        dialkylacrylamide, N,N-dialkylmethacrylamide, isoprene, butadiene, ethylene, vinyl acetate  
6        and combinations thereof.

1        38. The mixture of claim 35, wherein n is greater than or equal to 10.

2               combining water, a first polymerizable monomer, initiating radical, control  
3       agent and, optionally surfactant, to form a polymerization system;  
4               subjecting said polymerization system to polymerization conditions thereby  
5       forming a first polymer segment;  
6               adding a second polymerizable monomer to said polymerization system under  
7       polymerization conditions thereby forming a second polymer segment attached to said first  
8       polymer segment to form a block copolymer; and  
9               wherein either said first polymer segment or said second polymer segment has  
10      a weight average molecular weight of greater than or equal to about 25,000.

1               43. A heterogeneous free radical polymerization process comprising:  
2               forming a seed;  
3               loading said seed with either (1) a composition comprised of initiating radical  
4       and control agent or (2) an initiator-control agent adduct; and  
5               polymerizing a heterogeneous mixture with said loaded seed.

1               44. The process of claim 43, wherein said seed has a hydrodynamic radius of less than  
2       or equal to about 50 nanometers.

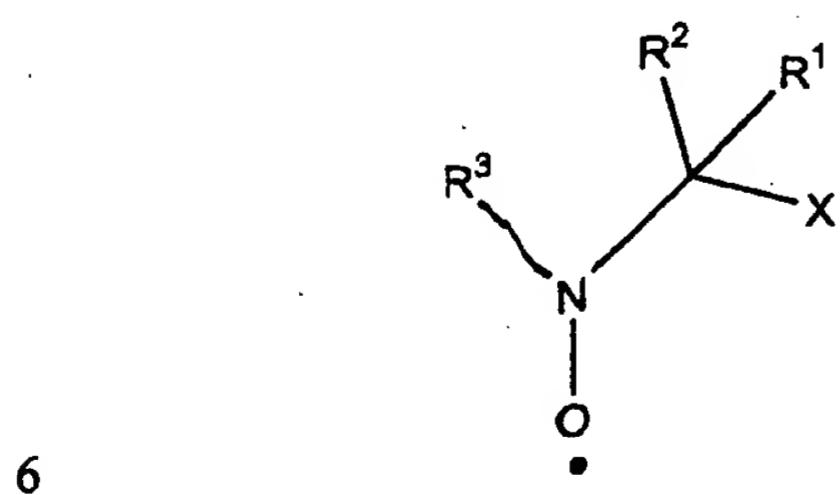
1               45. A heterogeneous free radical polymerization process comprising:  
2               forming a first mixture comprised of a first polymerizable monomer, initiator,  
3       water and surfactant, wherein said first polymerizable monomer comprises no more than 10%  
4       by weight of said first mixture;  
5               subjecting said first mixture to polymerization conditions to give a first  
6       heterogeneous polymerization;  
7               ending said first heterogeneous polymerization to provide a seed, and  
8       optionally recovering said seed;  
9               forming a second mixture comprised of said seed, water and either (1) a  
10      composition comprised of an initiator and control agent or (2) an initiator-control agent  
11      adduct;  
12               optionally maintaining said second mixture for a sufficient time for either of  
13      said composition or said adduct to migrate into said seed;

2 combining water, at least one monomer, seed, initiating radical, control agent  
3 and, optionally surfactant, to form a polymerization system;  
4 subjecting said polymerization system to polymerization conditions, which  
5 includes a polymerization temperature of about 110°C or less.

1 50. A method for forming a polymer emulsion, comprising  
2 combining water, seed, at least one monomer, initiating radical, control agent  
3 and, optionally surfactant, to form a polymerization system;  
4 subjecting said polymerization system to polymerization conditions thereby  
5 forming polymer particles in emulsion; and  
6 controlling the hydrodynamic radius of said particles so that said particles  
7 have a hydrodynamic radius of about 150 nm or less and a second cumulant analysis PDI in  
8 the range of from about 0 to about 0.3.

1 51. A loaded seed useful in a controlled free radical emulsion polymerization  
2 comprising,  
3 polymer chains that are generally un-reactive in a free radical polymerization;  
4 and  
5 either (1) a composition comprised of initiating radical and control agent or (2)  
6 an initiator-control agent adduct.

1 52. A loaded seed useful in a controlled free radical emulsion polymerization  
2 comprising,  
3 polymer chains that are un-reactive in a free radical polymerization; and  
4 a composition comprised of initiating radical and control agent said control  
5 agent being characterized by the general formula:



3           a first mixture comprised of a first polymerizable monomer, initiator, water  
 4   and surfactant, wherein said first polymerizable monomer comprises no more than 10% by  
 5   weight of said first mixture;

6           subjecting said first mixture to polymerization conditions to give a first  
 7   heterogeneous polymerization;

8           ending said first heterogeneous polymerization to provide a seed, and  
 9   optionally recovering said seed;

10          forming a second mixture comprised of said seed, water and either (1) a  
 11   composition comprised of an initiator and control agent or (2) an initiator-control agent  
 12   adduct; and

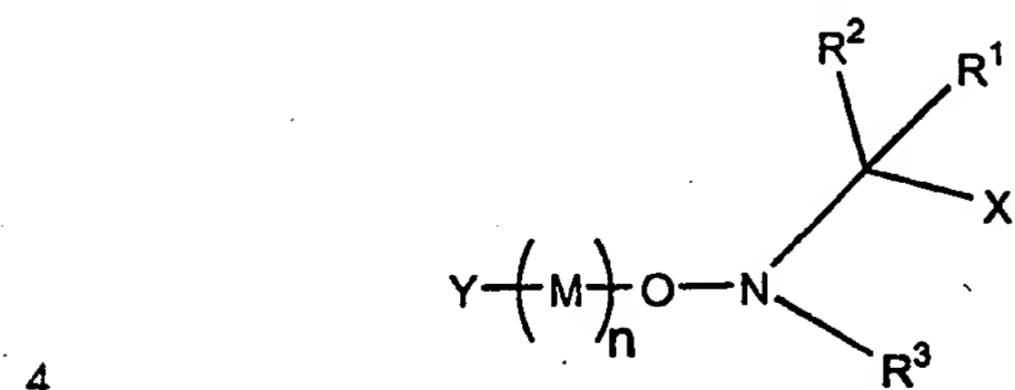
13          optionally maintaining said second mixture for a sufficient time for either of  
 14   said composition or said adduct to migrate into said seed.

1           55. A method for loading seeds, which are useful in a heterogeneous polymerization,  
 2   comprising:

3           forming a mixture comprised of a seed, water, organic solvent, base and either  
 4   (1) a composition comprised of an initiator and control agent or (2) an initiator-control agent  
 5   adduct; and

6           maintaining said mixture for a sufficient time for either of said composition or  
 7   said adduct to migrate into said seed.

1           56. A heterogeneous mixture comprising a plurality of particles, the particles  
 2   comprising polymer chains that are generally un-reactive in a free radical polymerization and  
 3   a compound characterized by the formula:



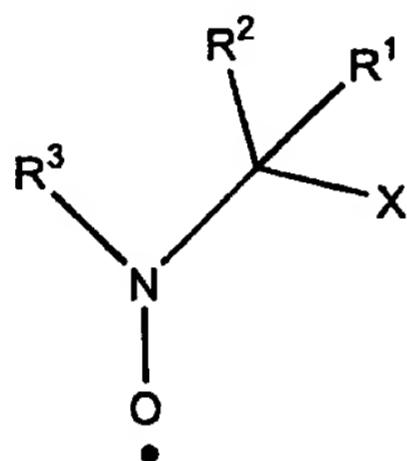
5           where X is a moiety that is capable of destabilizing said control agent on a  
 6   polymerization time scale, Y is a moiety capable of initiating a free radical polymerization;

1        63. The block copolymer of claim 62, wherein the first and second segments are  
 2        selected from different classes of the set of classes consisting of styrene, substituted styrene,  
 3        acrylates, methacrylates, acrylamides, methacrylamides, N-vinyl and O-vinyl compounds.

1        64. The block copolymer of claim 62, wherein the block copolymer is an amphiphilic  
 2        block copolymer.

1        65. The block copolymer of claim 62, wherein the block copolymer is a hard/soft  
 2        block copolymer.

1        66. A method for polymerizing comprising  
 2                combining water, initiator, at least one monomer and nitroxide radical into a  
 3        polymerization system, said radical being characterized by the general formula:



4        5        where X is a moiety that is capable of destabilizing said control agent on a  
 6        polymerization time scale; and

7        8        9        10        11        12        each R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of alkyl,  
 substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted  
 heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy,  
 silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally R<sup>1</sup> and R<sup>2</sup>  
 are joined together in a ring structure; also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in a ring  
 structure, and

13        14        subjecting said polymerization system to polymerization conditions; wherein said at  
 least one monomer is water soluble or miscible in water.

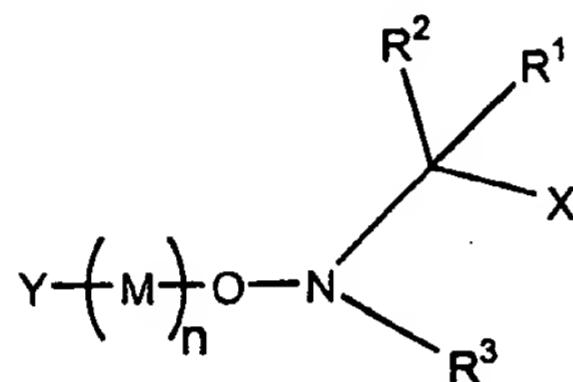
1        67. The method of claim 66, wherein said initiator and control agent are soluble in the  
 2        water and at least one monomer solution.

9 silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally R<sup>1</sup> and R<sup>2</sup>  
 10 are joined together in a ring structure; also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in a ring  
 11 structure;

12 M is one or more monomers; and n is an integer greater than or equal to 0.

1 70. A block copolymer prepared by the method of either of claims 66 or 68, wherein  
 2 at least one polymer segment of said block copolymer has a weight average molecular weight  
 3 of greater than or equal to 25,000.

1 71. A water soluble polymer characterized by the formula:



3 where X is hydrogen;

4 each R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of alkyl,  
 5 substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted  
 6 heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy,  
 7 silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; optionally R<sup>1</sup> and R<sup>2</sup>  
 8 are joined together in a ring structure; also optionally R<sup>2</sup> and R<sup>3</sup> are joined together in a ring  
 9 structure;

10 Y is a residue derived from a species that initiates free radical polymerization or is  
 11 selected from the group consisting of alkyl, substituted alkyl, alkoxy, substituted alkoxy, aryl,  
 12 and substituted aryl;

13 M is selected from the group consisting of alkyl acrylate, substituted alkyl acrylate,  
 14 substituted alkyl methacrylate, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide,  
 15 N-alkylacrylamide, N-alkylmethacrylamide, N,N-dialkylacrylamide, N,N-  
 16 dialkylmethacrylamide, acrylic acid, and vinyl acetate; and n is an integer greater than 1.

1 72. A free radical emulsion polymerization process comprising:

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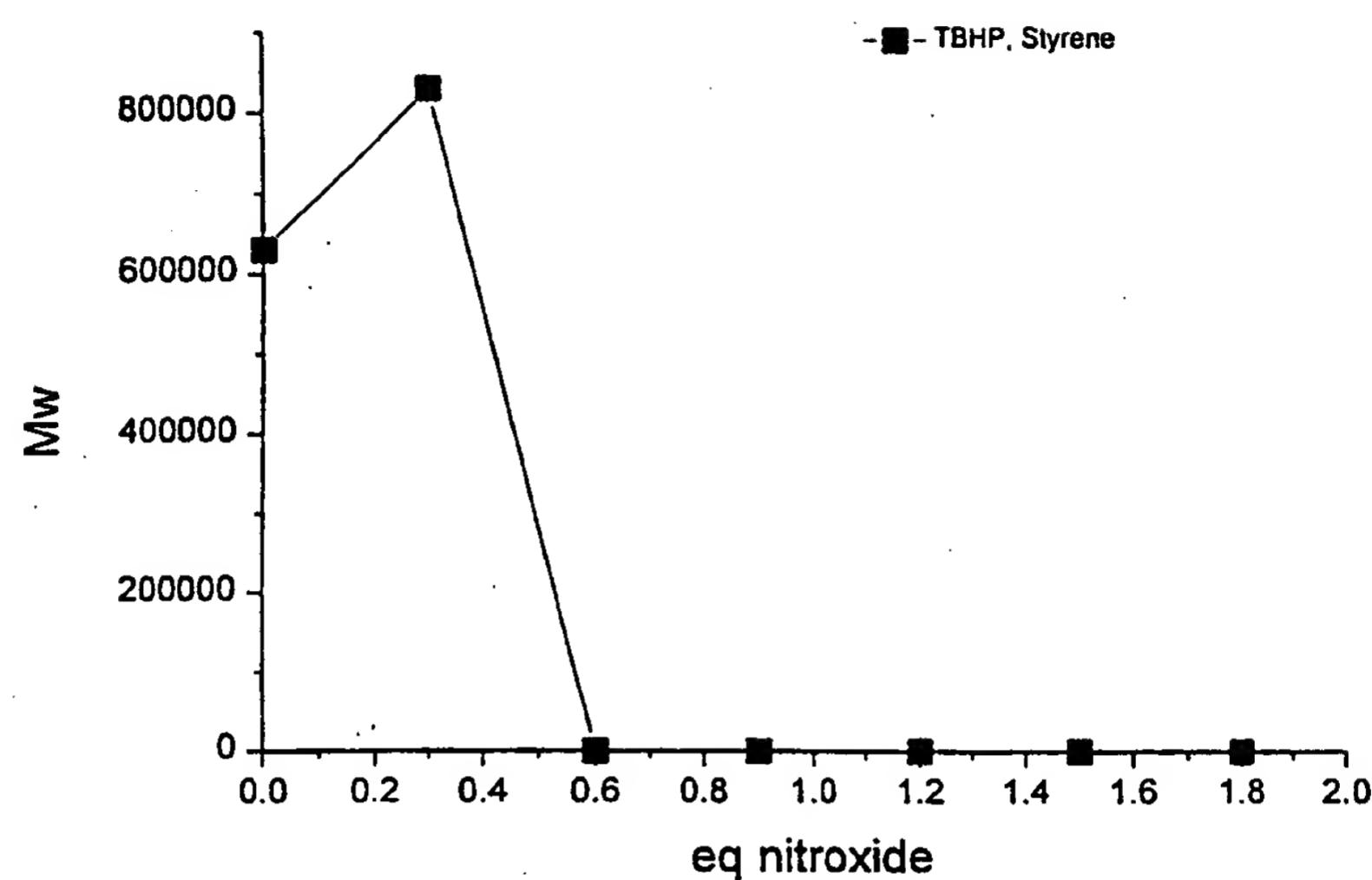


FIG. 1A

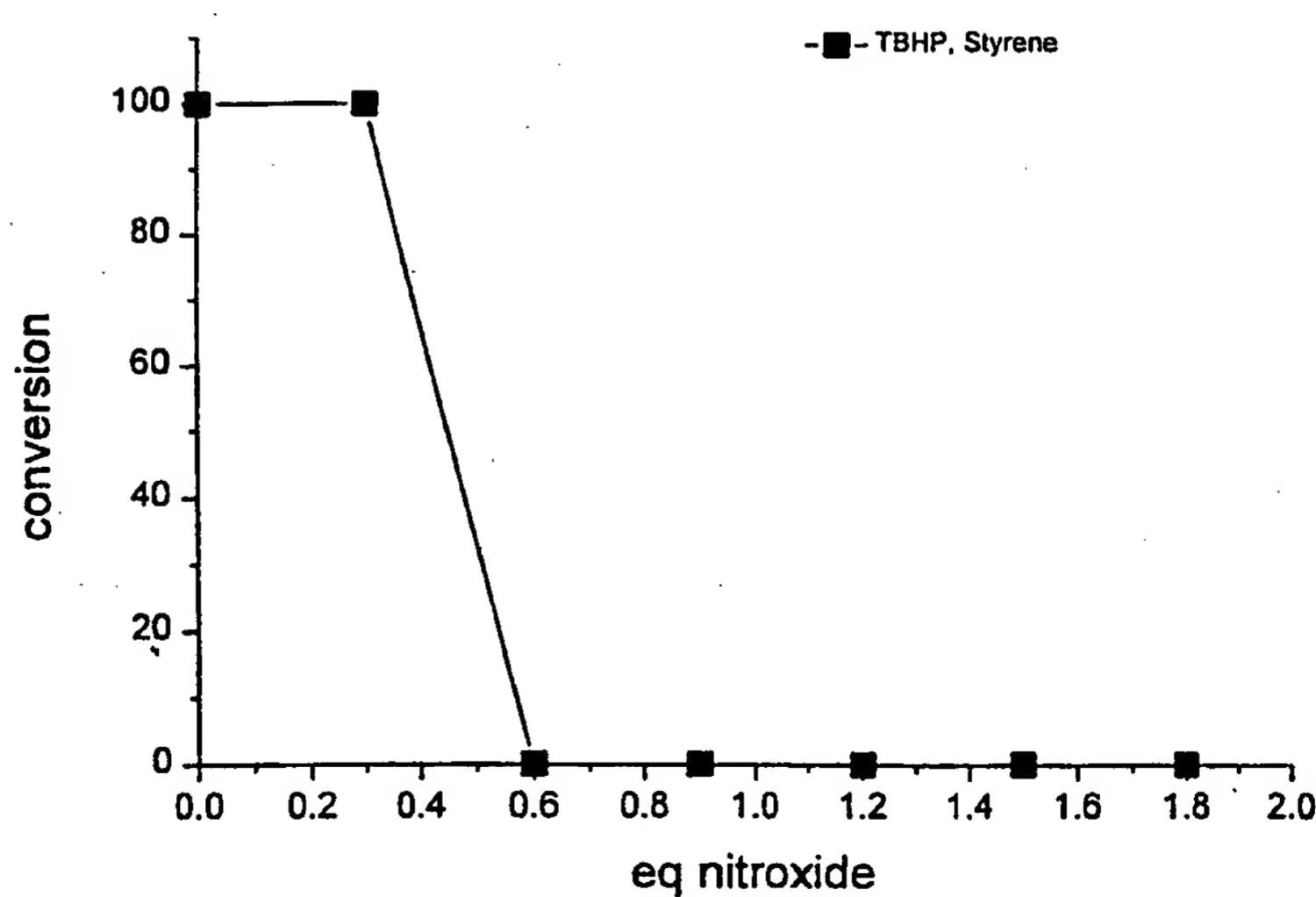


FIG. 1B

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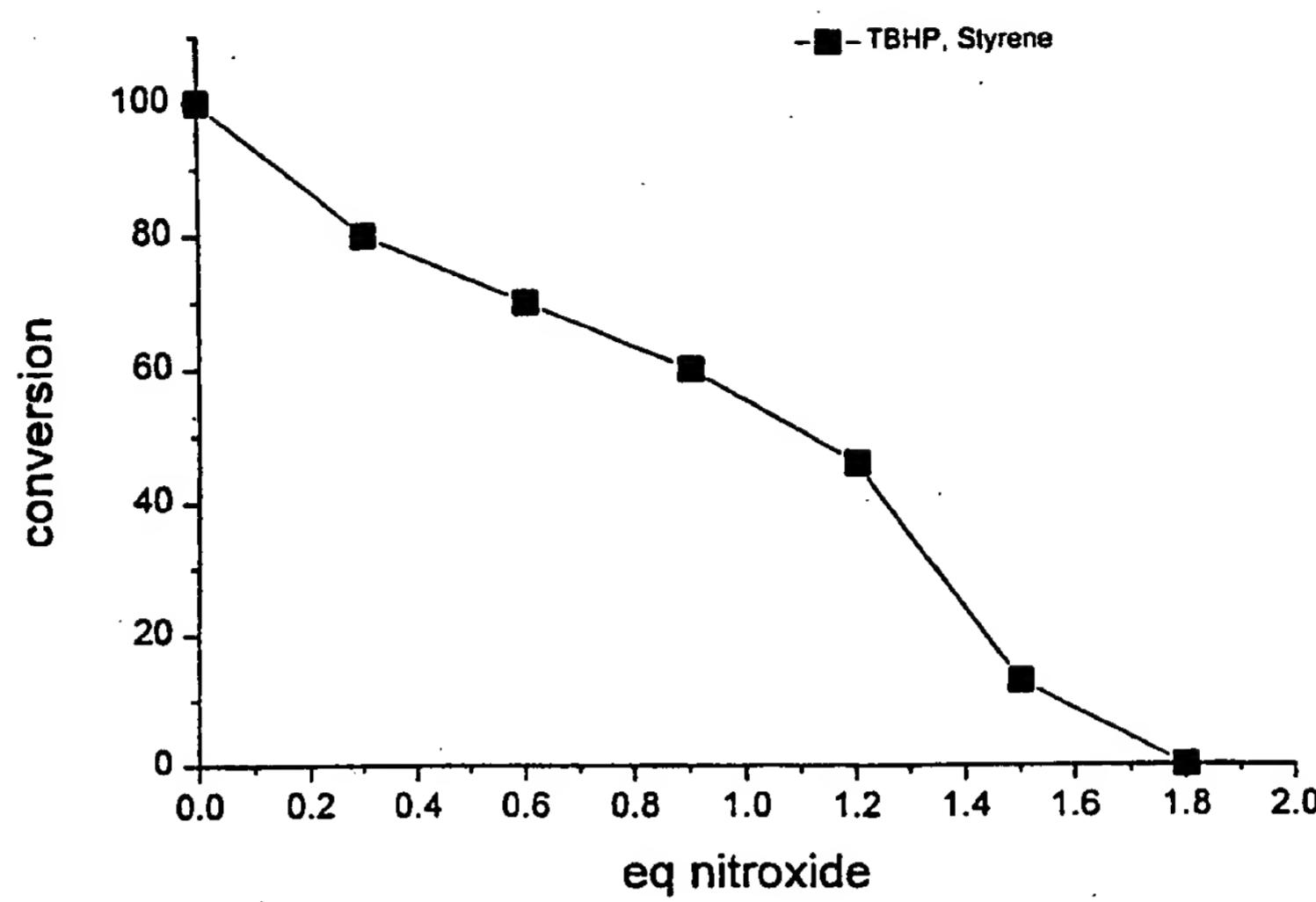


FIG. 2A

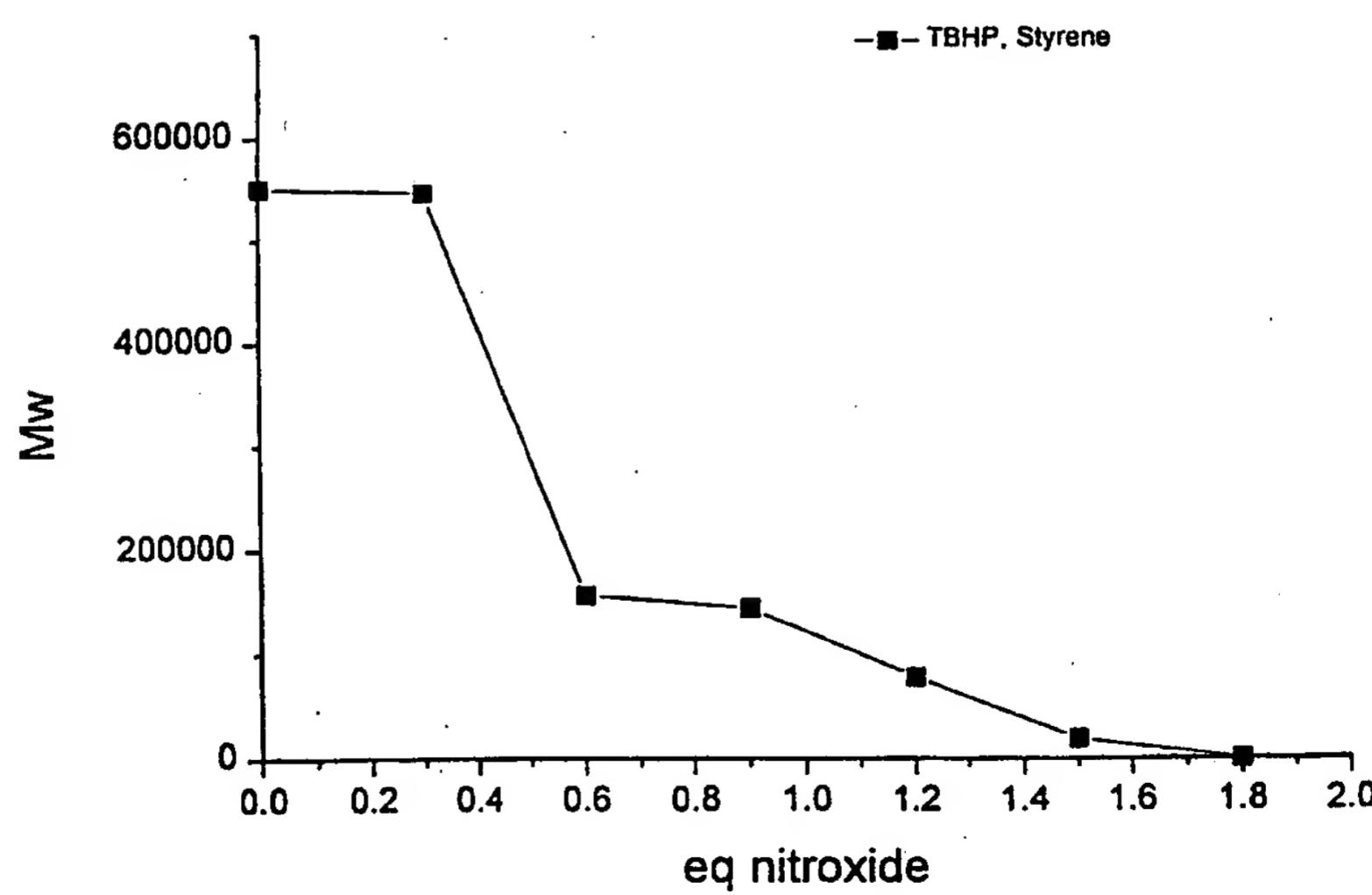


FIG. 2B

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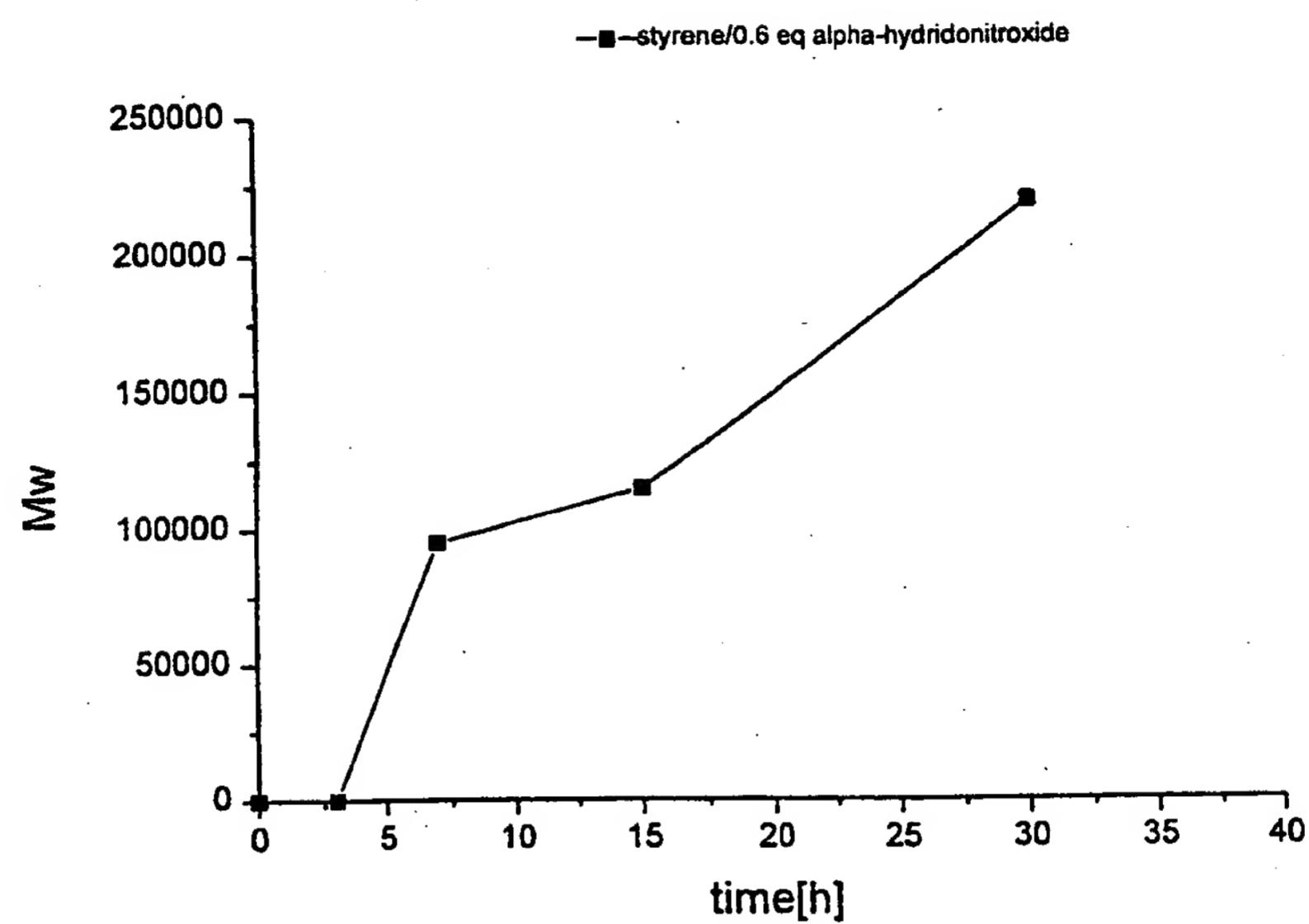


FIG. 3A

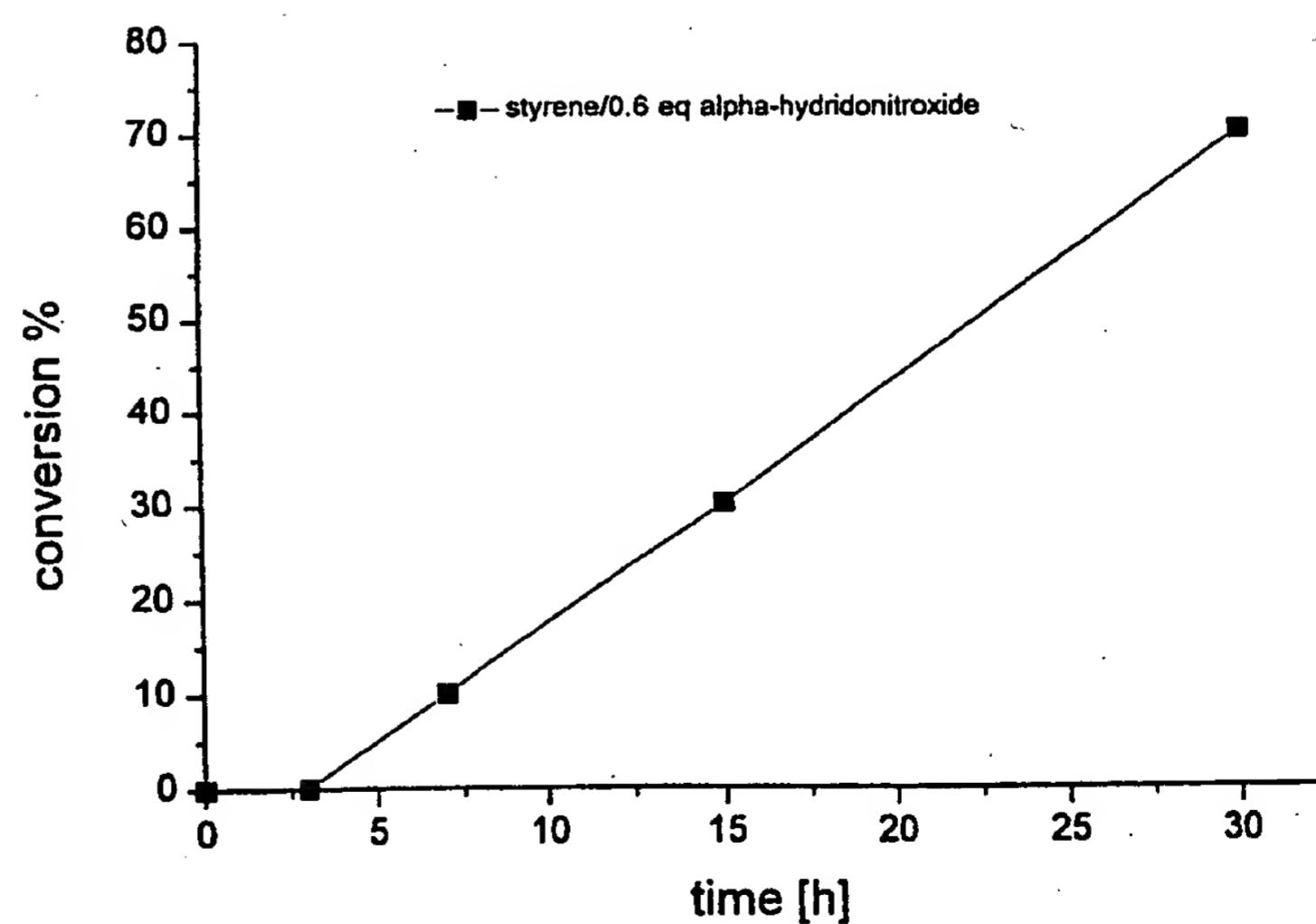


FIG. 3B

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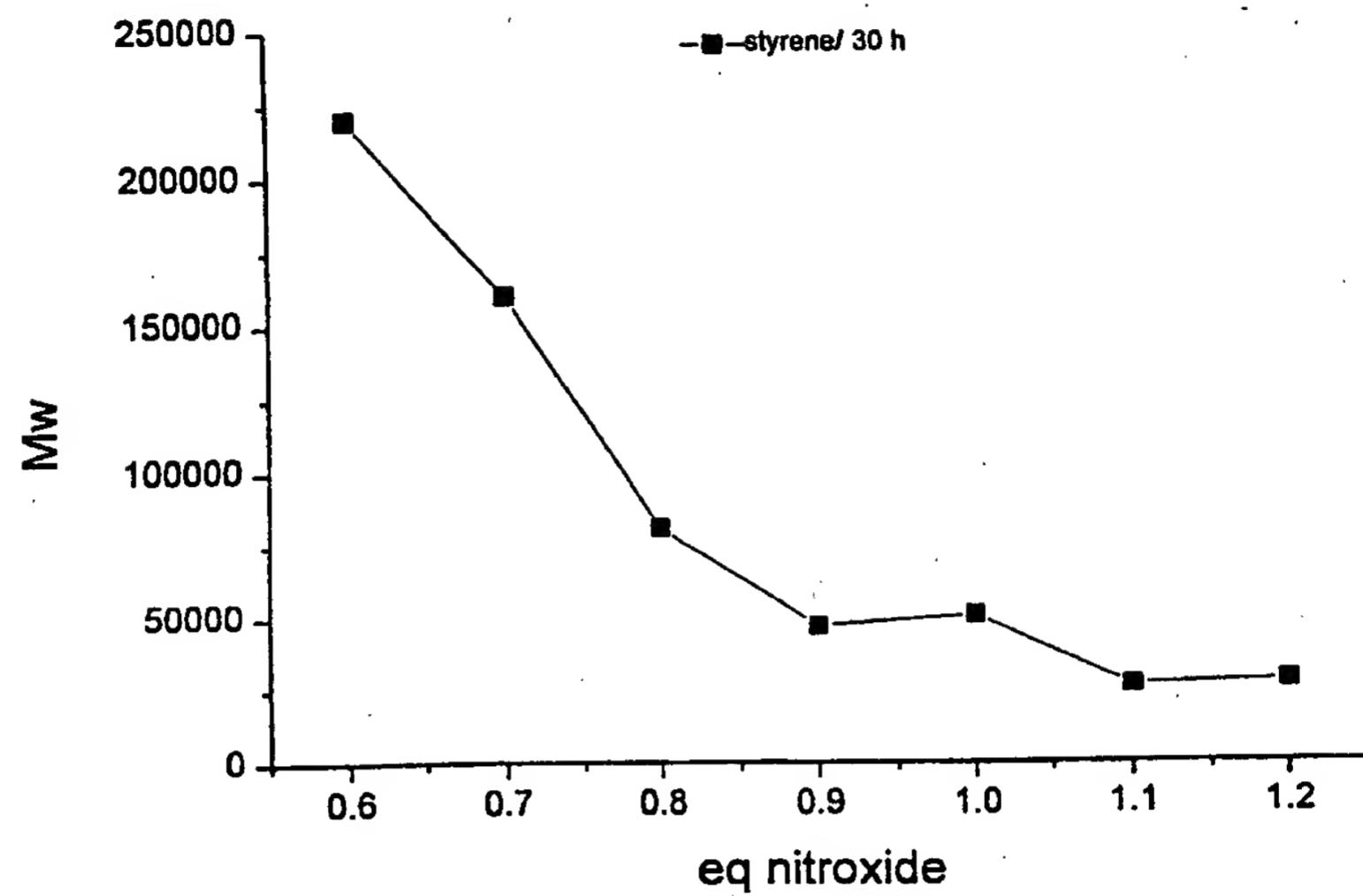


FIG. 3C

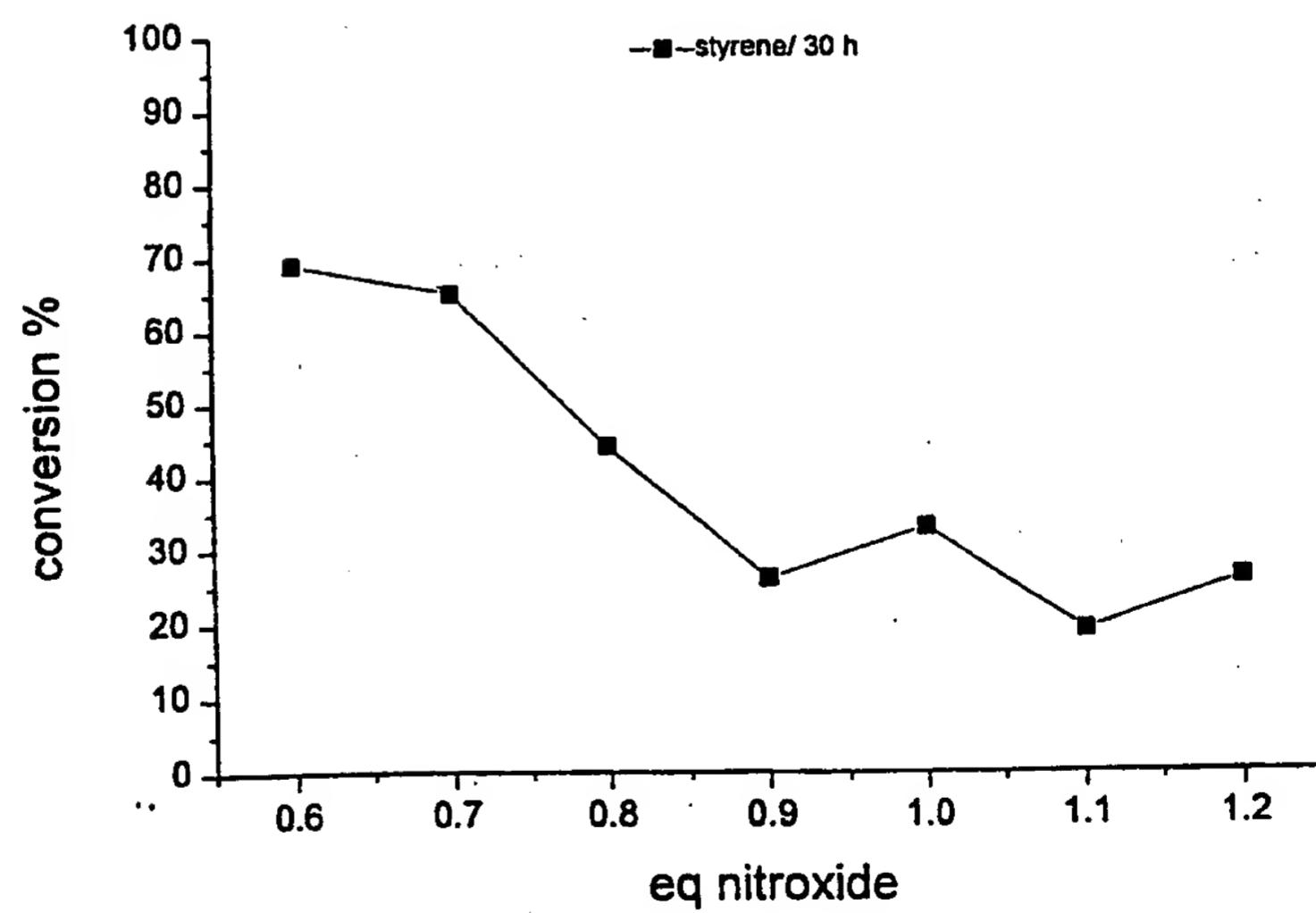


FIG. 3D

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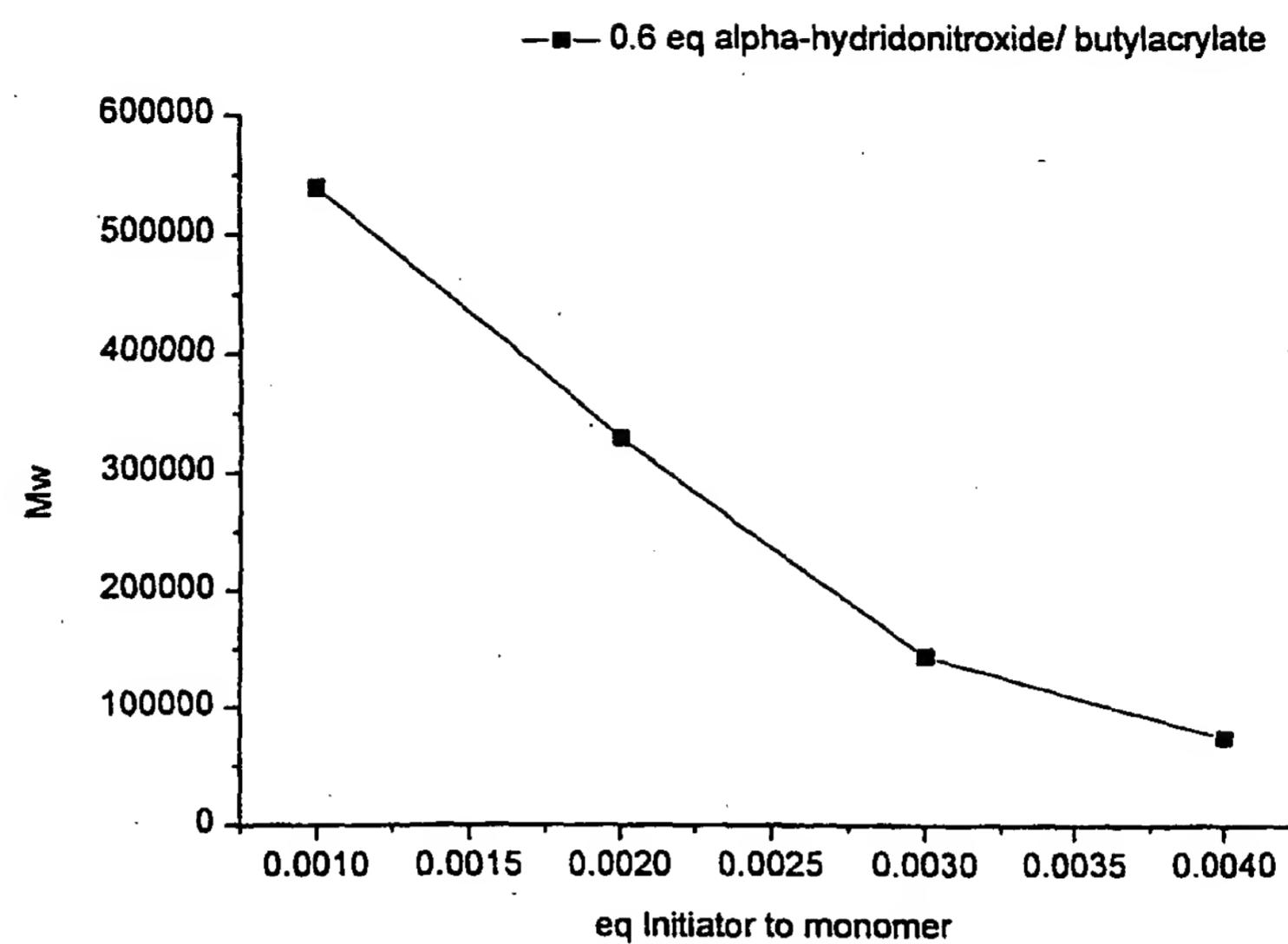


FIG. 3E

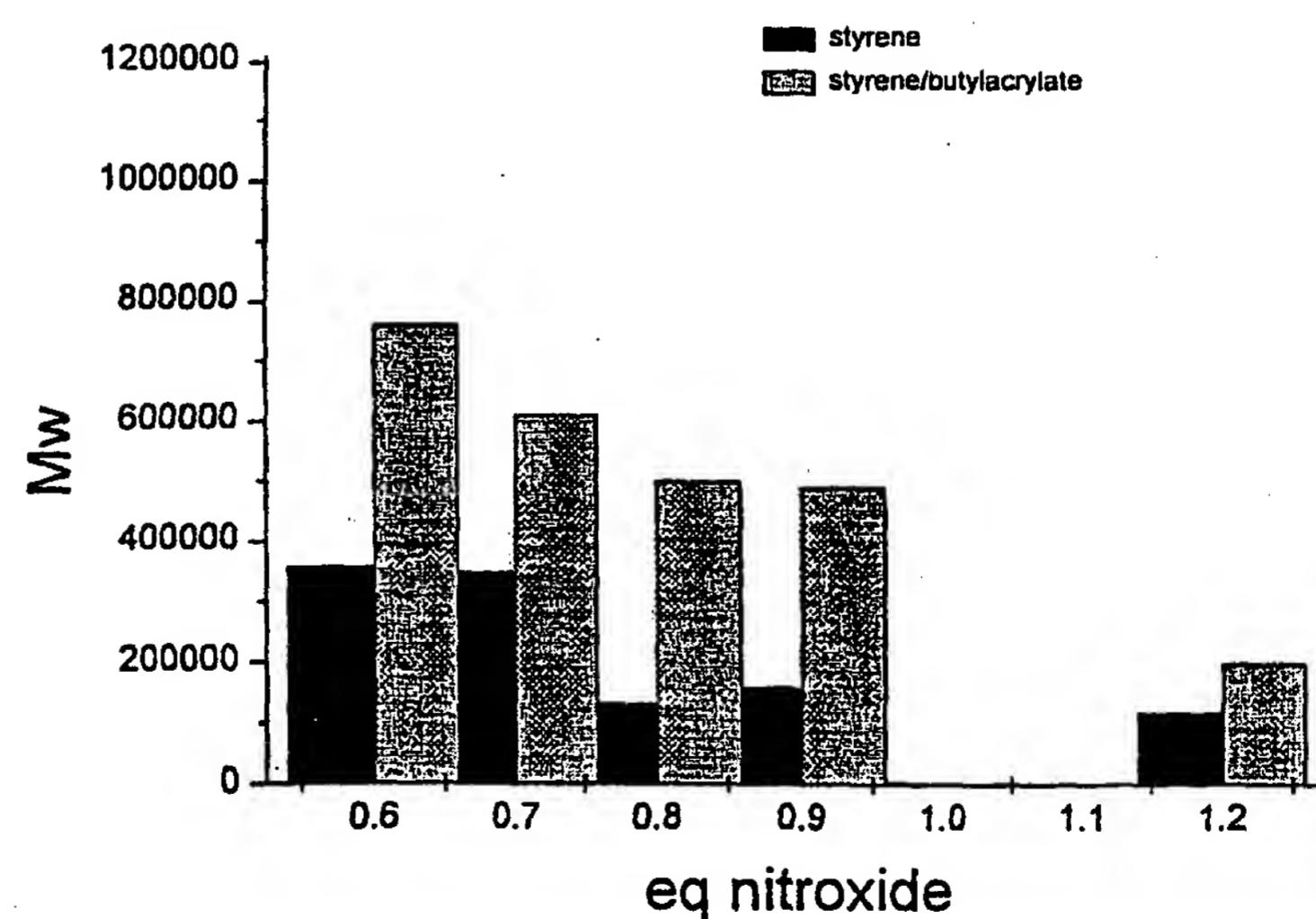


FIG. 4

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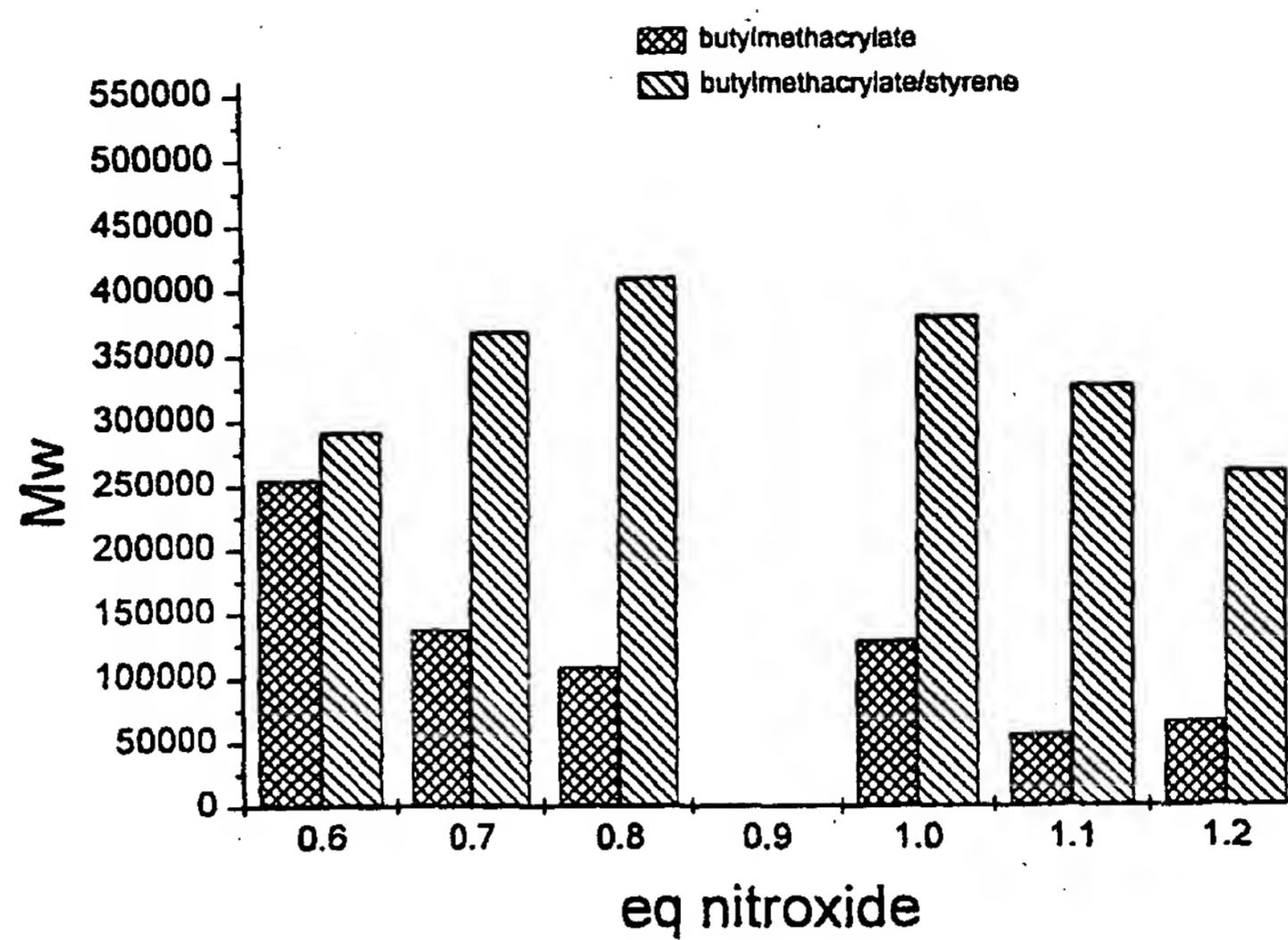


FIG. 5

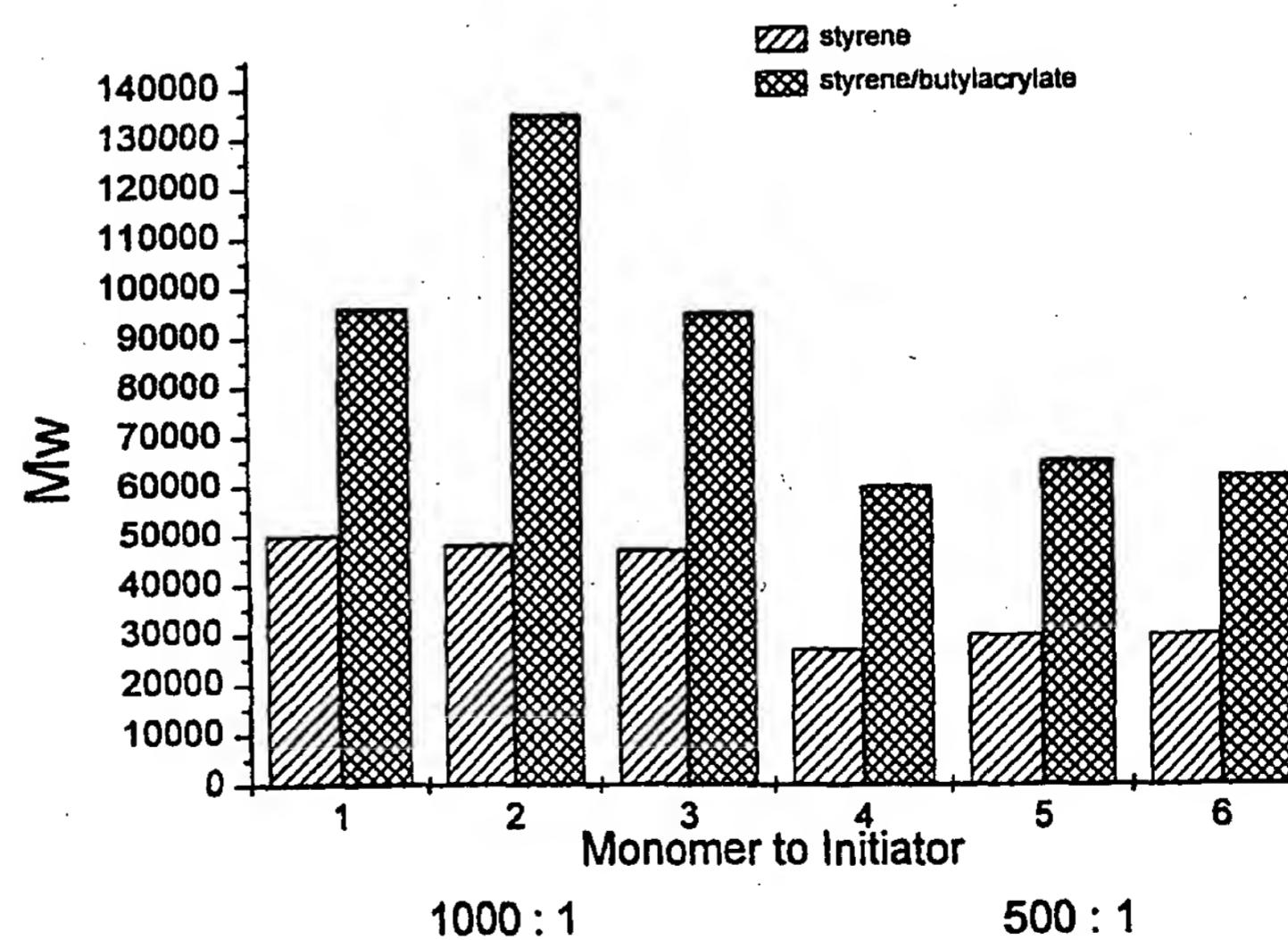


FIG. 6

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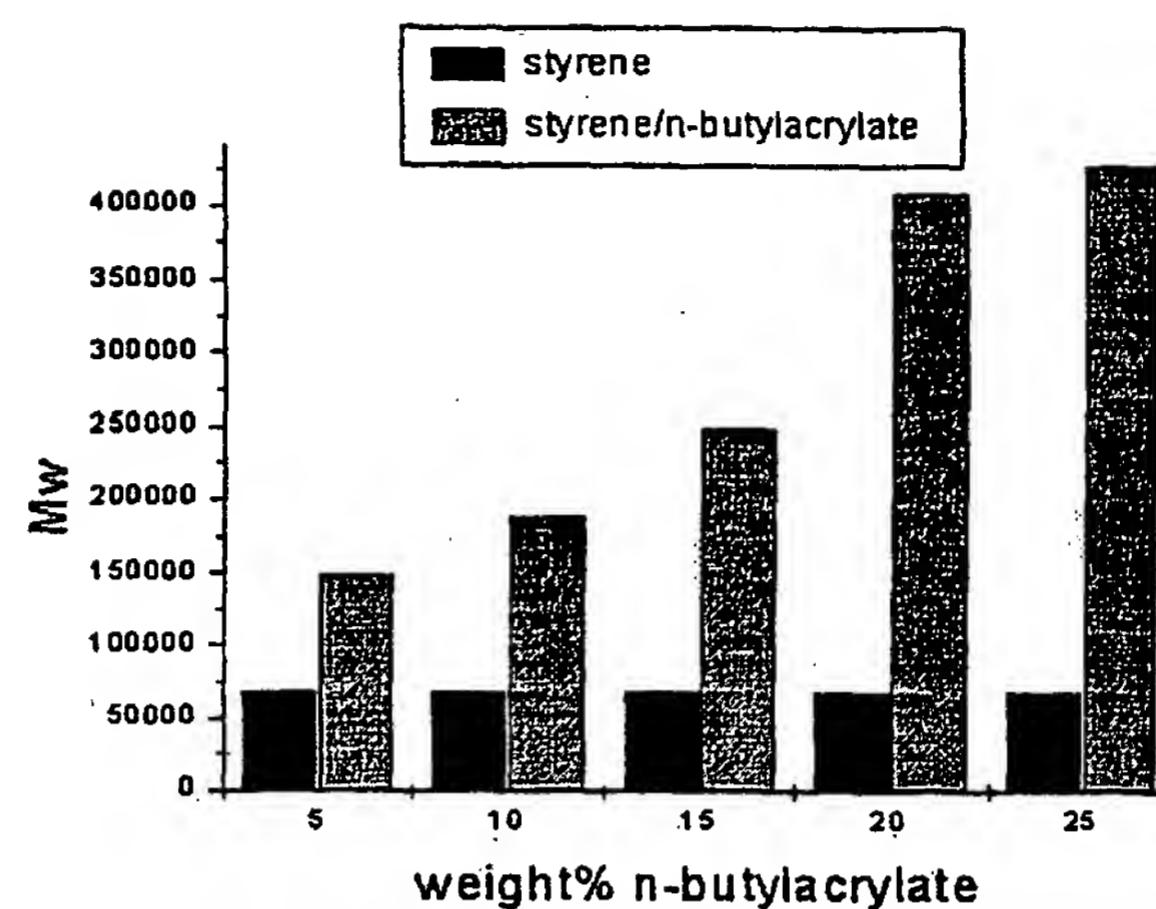


FIG. 7

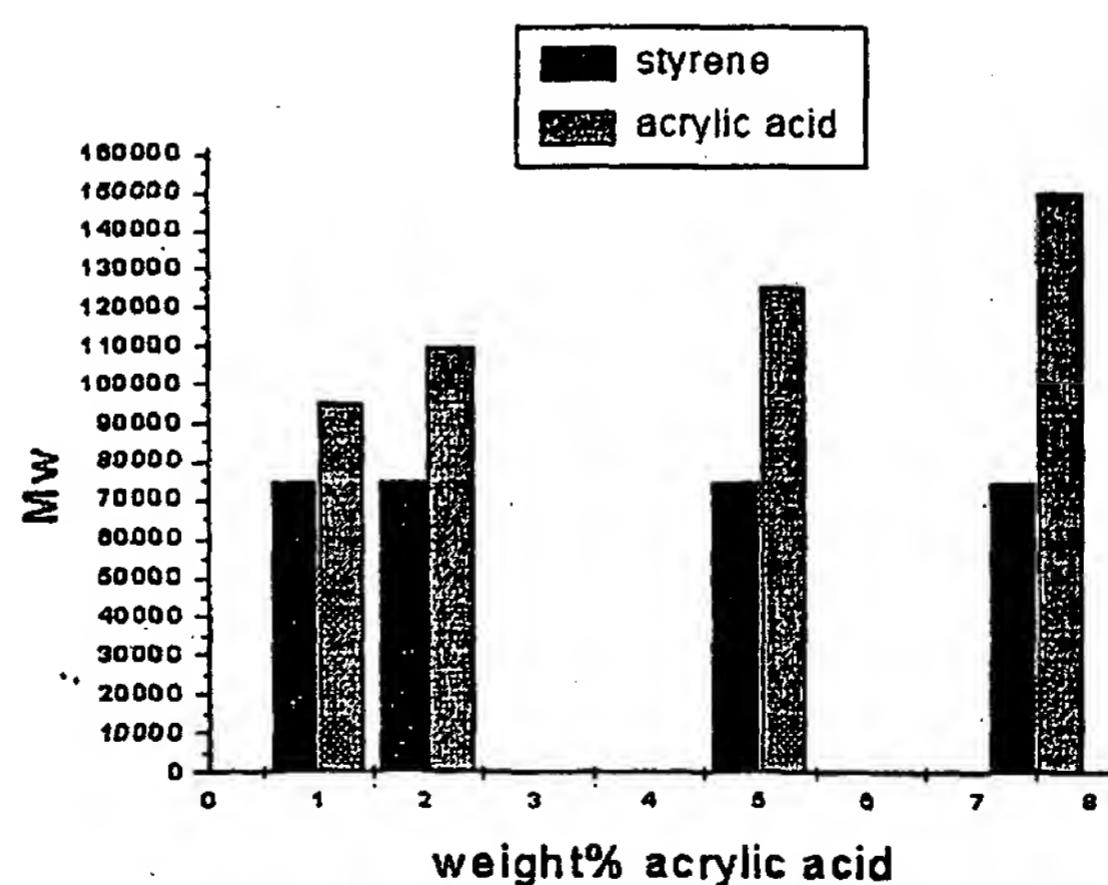


FIG. 8

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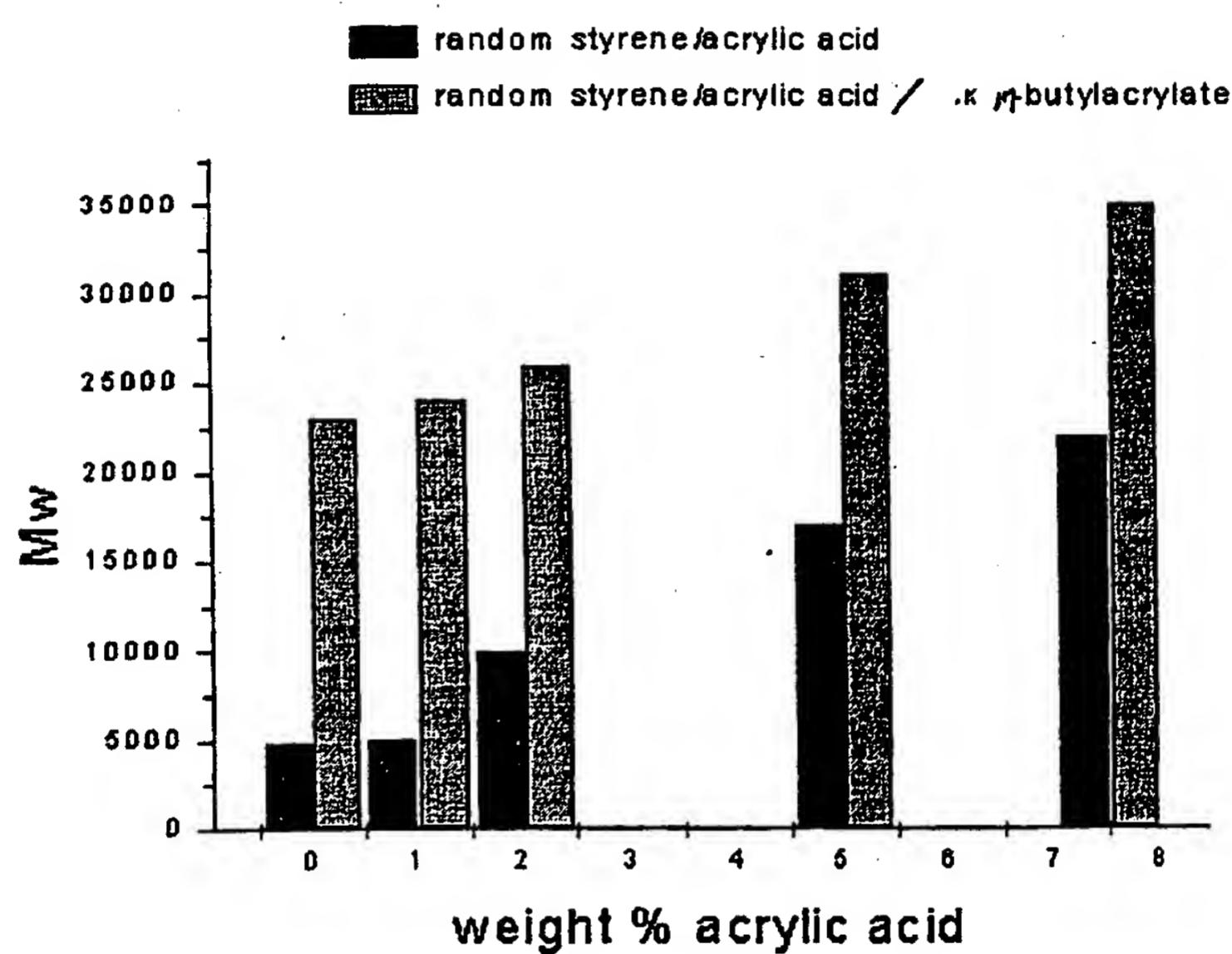


FIG. 9

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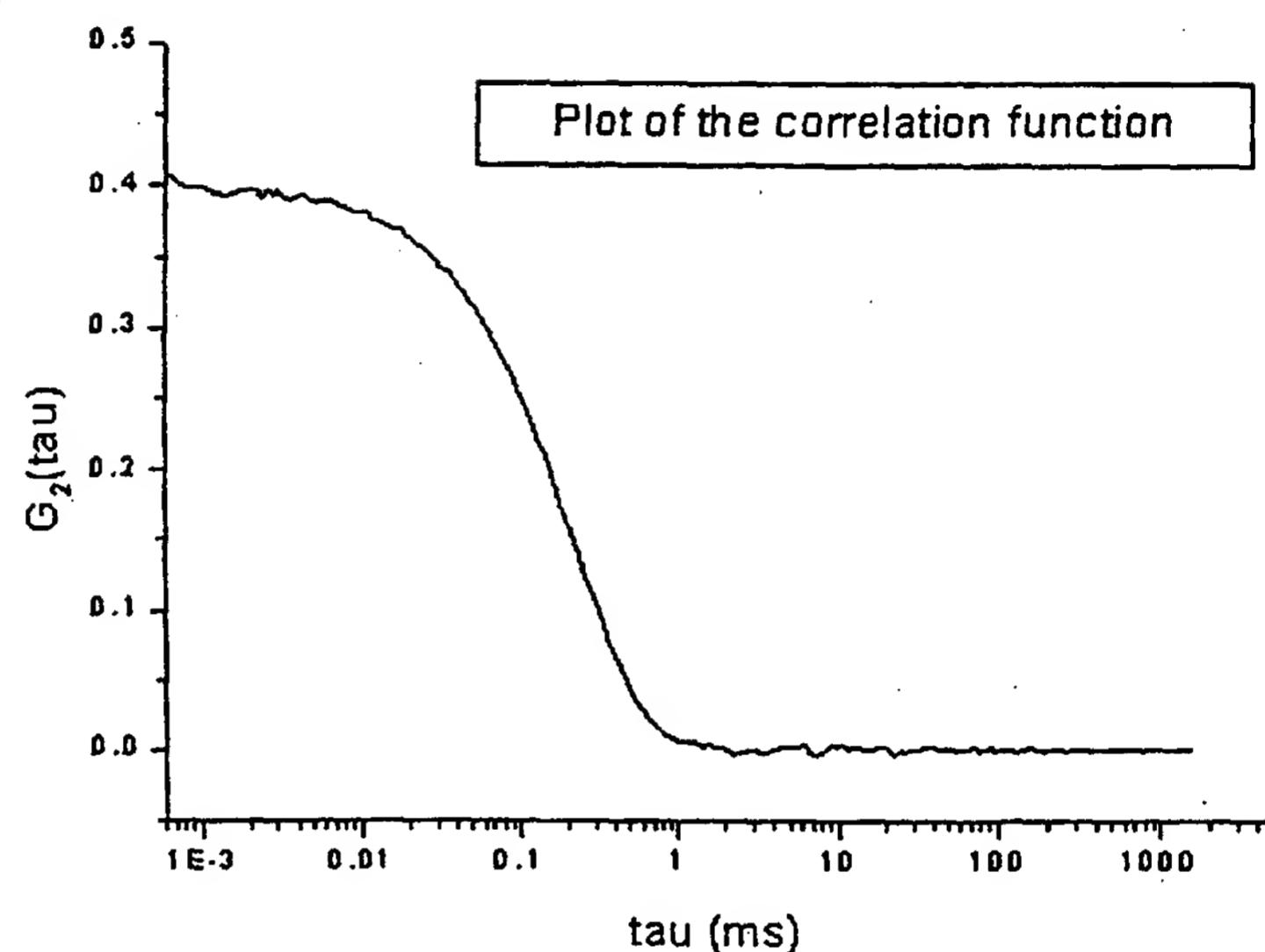


FIG. 10

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Polystyrene-poly(butyl acrylate)

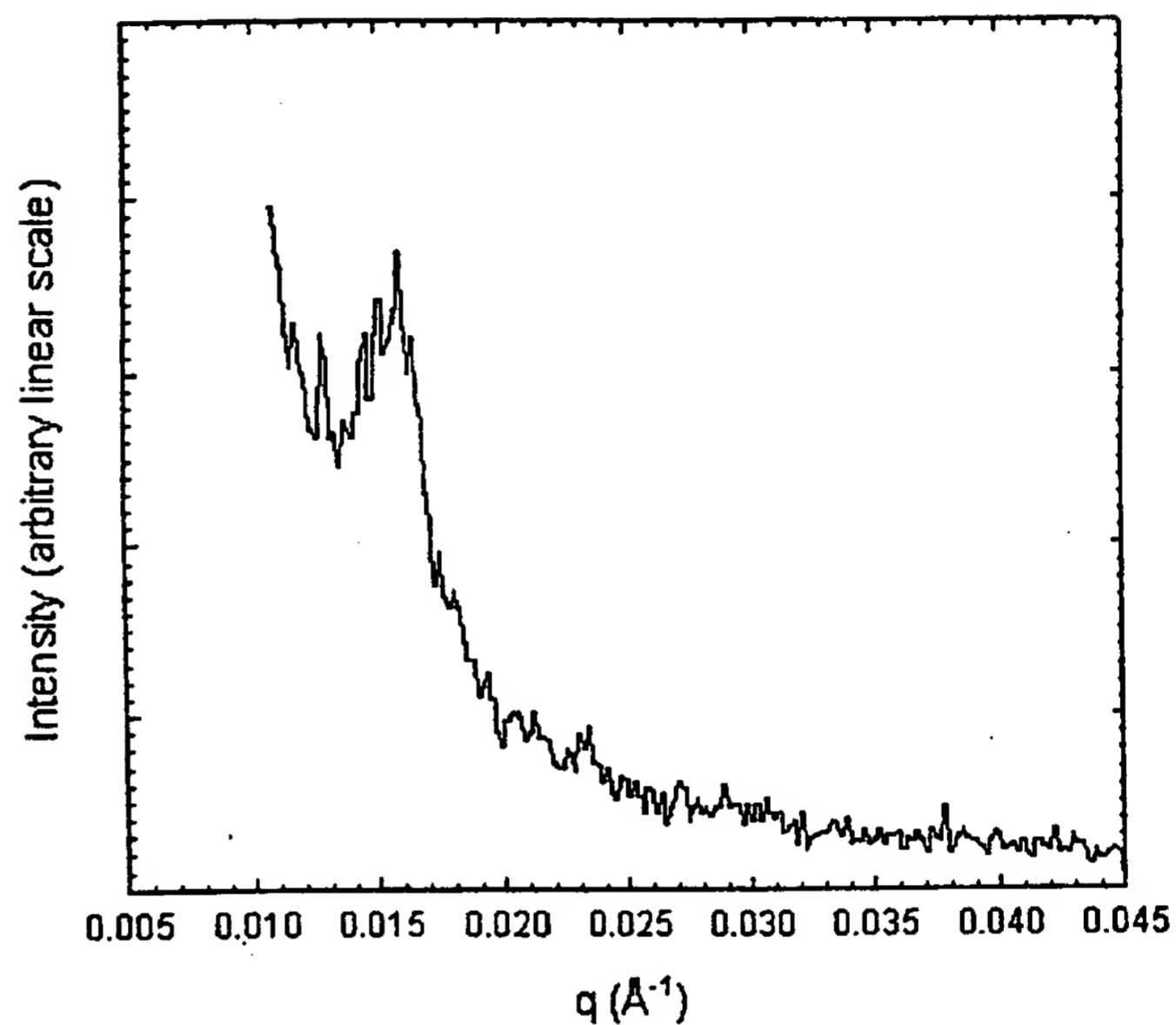


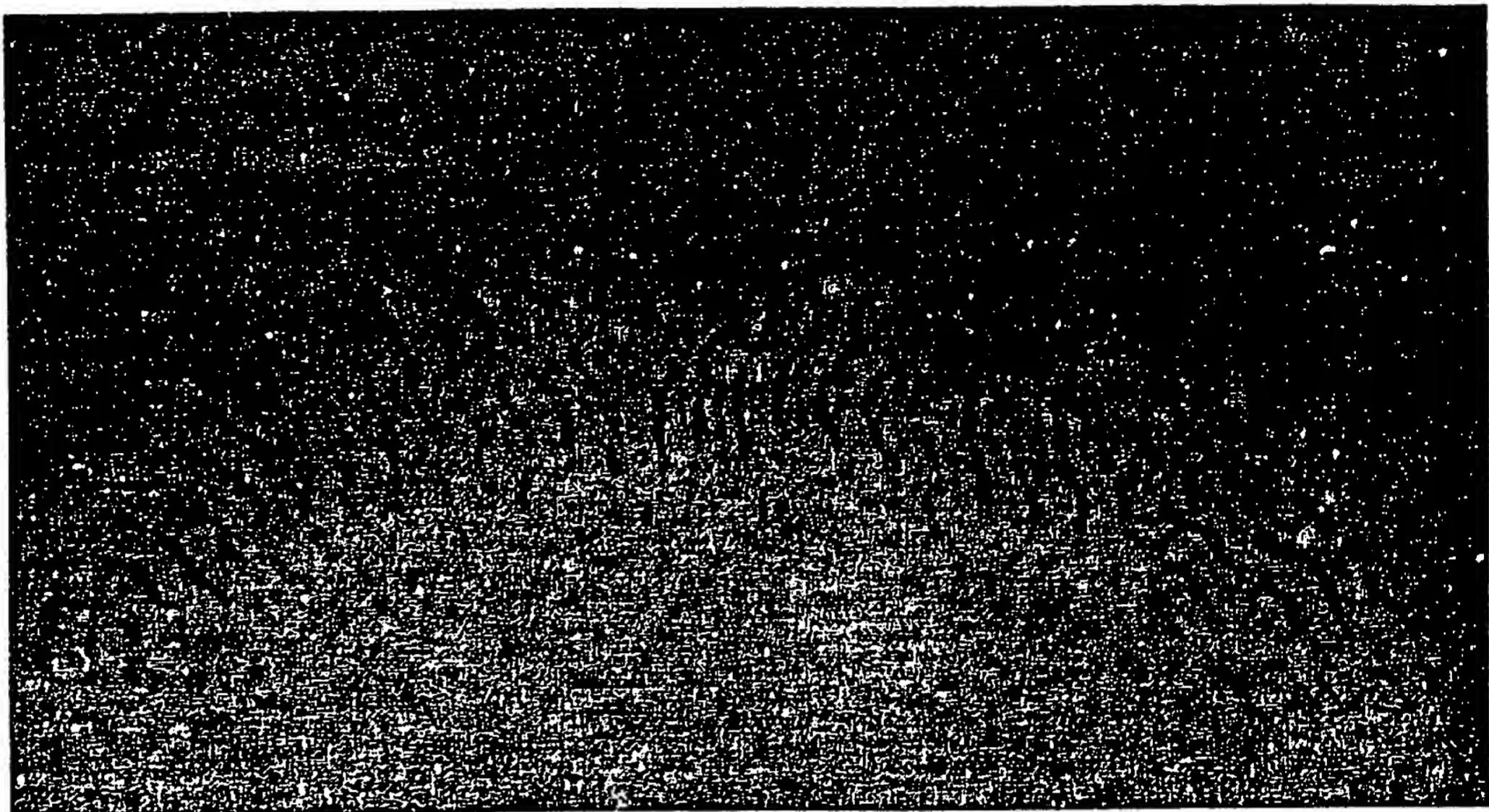
FIG. 11

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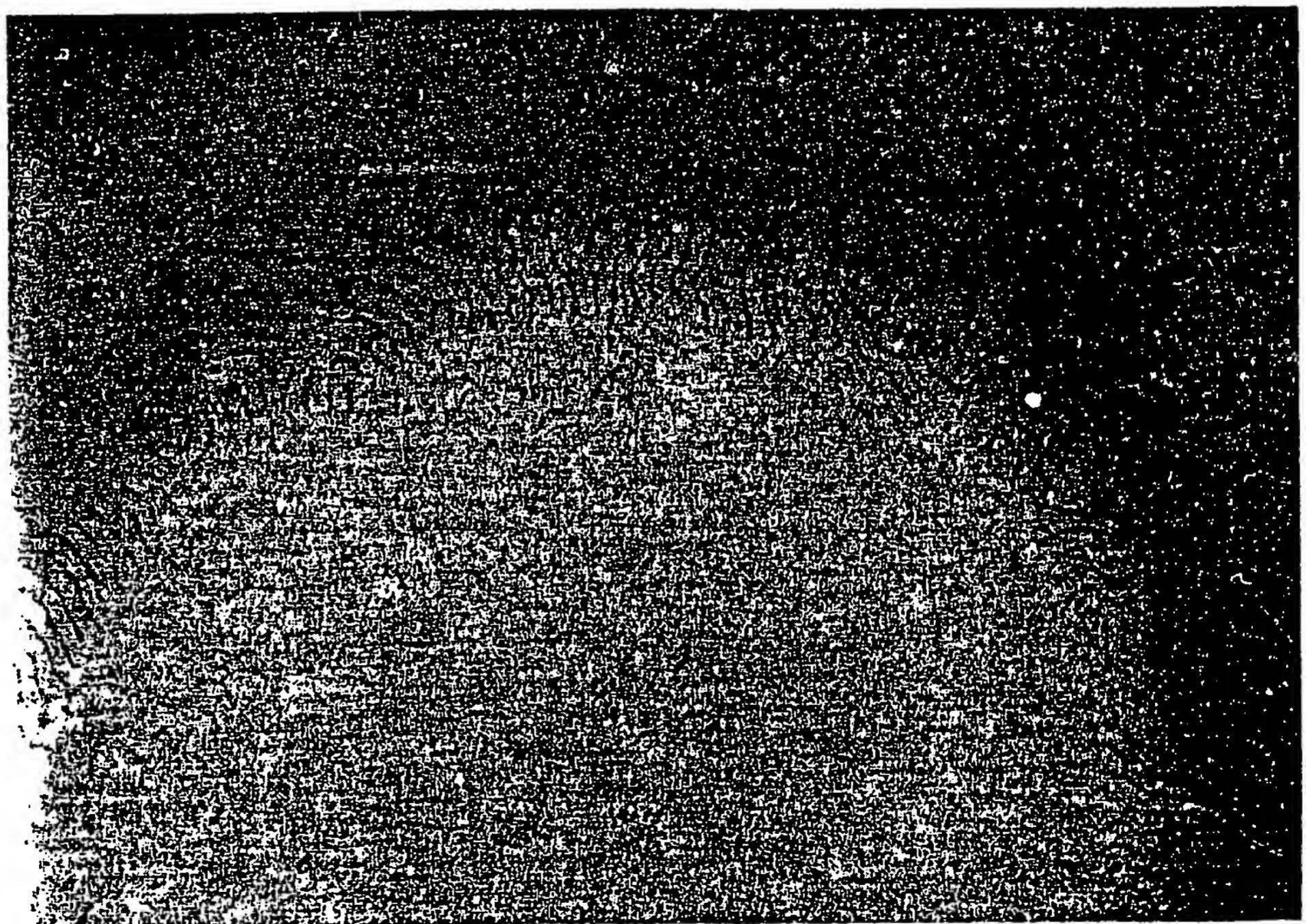


**FIG. 12**

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**FIG. 13A**



**FIG. 13B**

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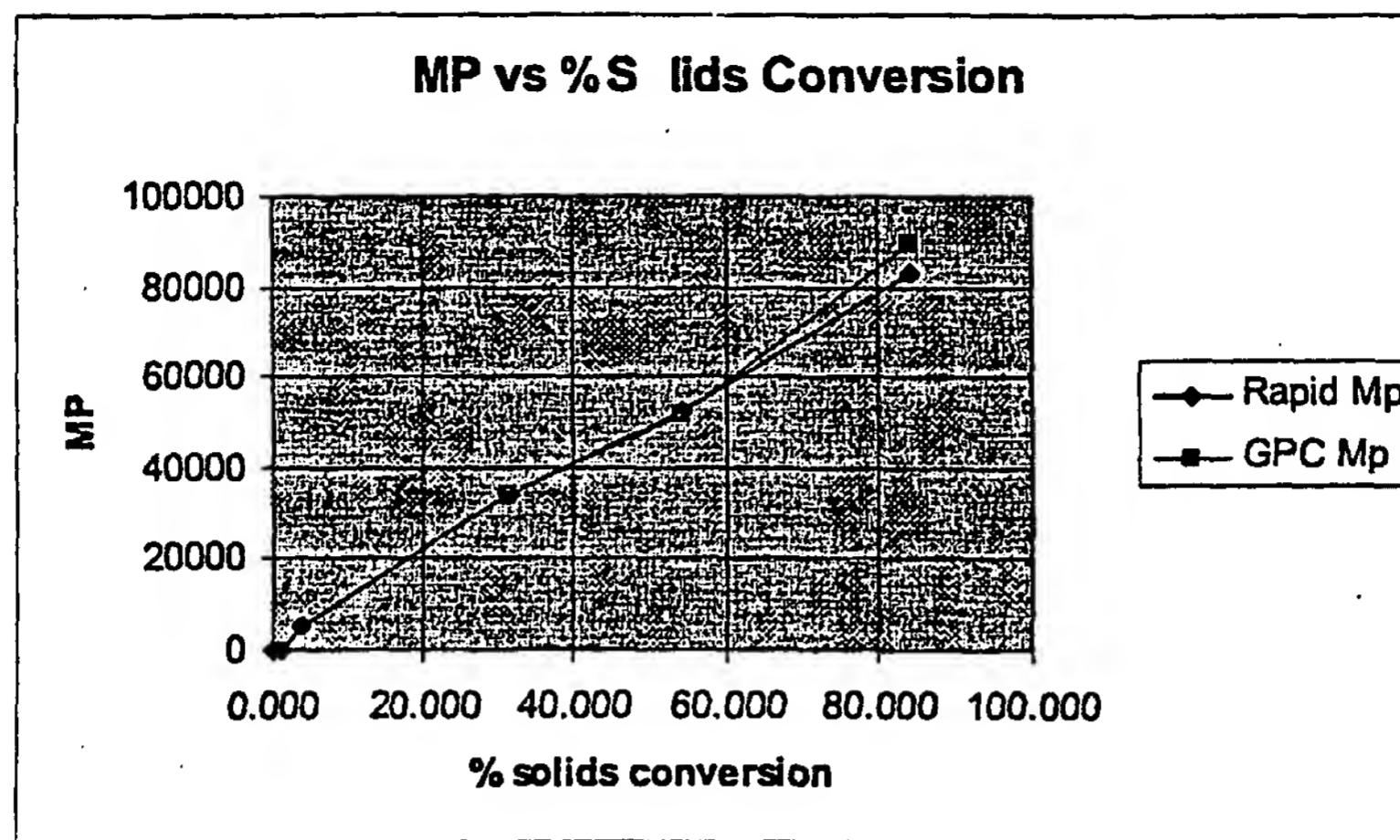


Fig. 14A

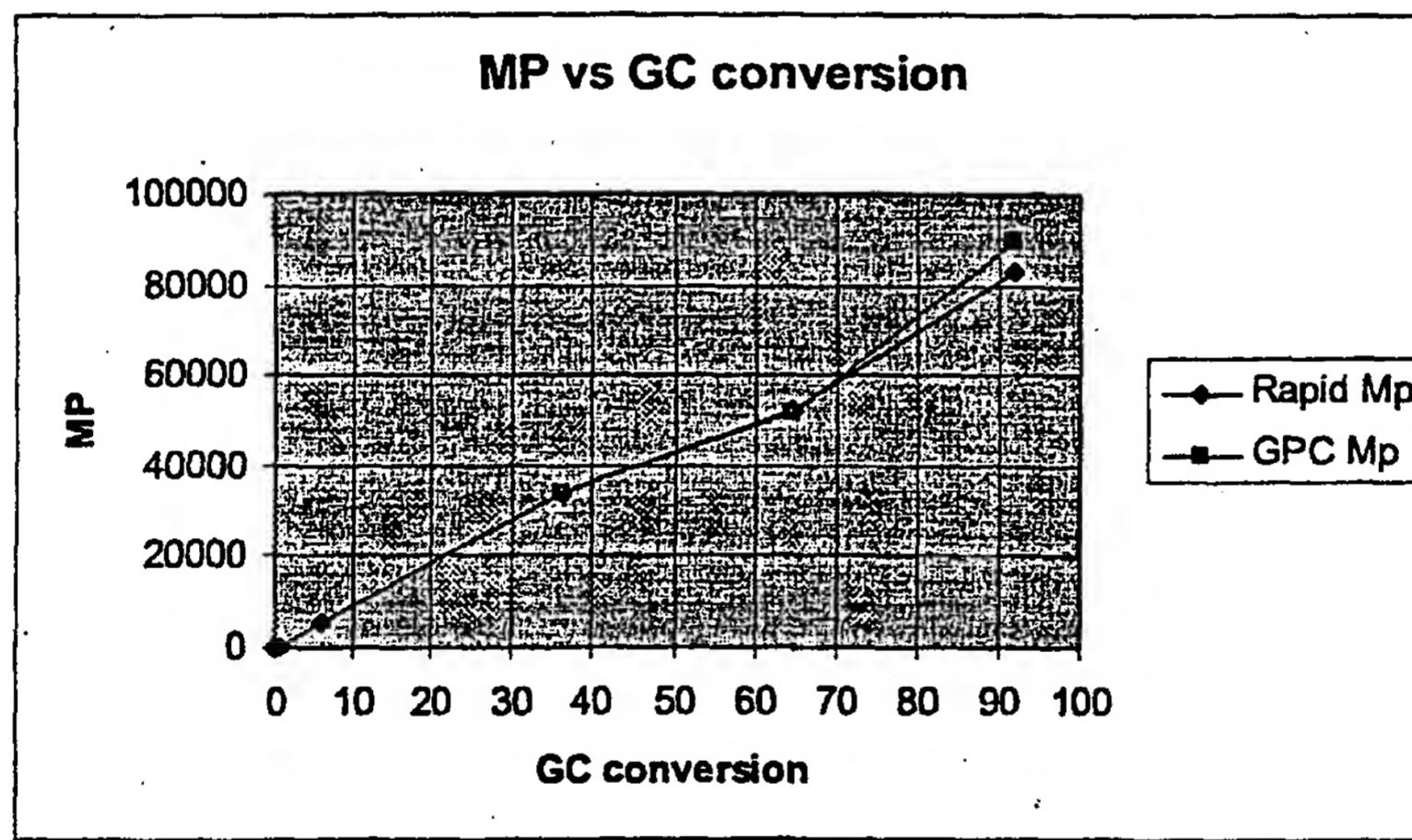


Fig. 14B

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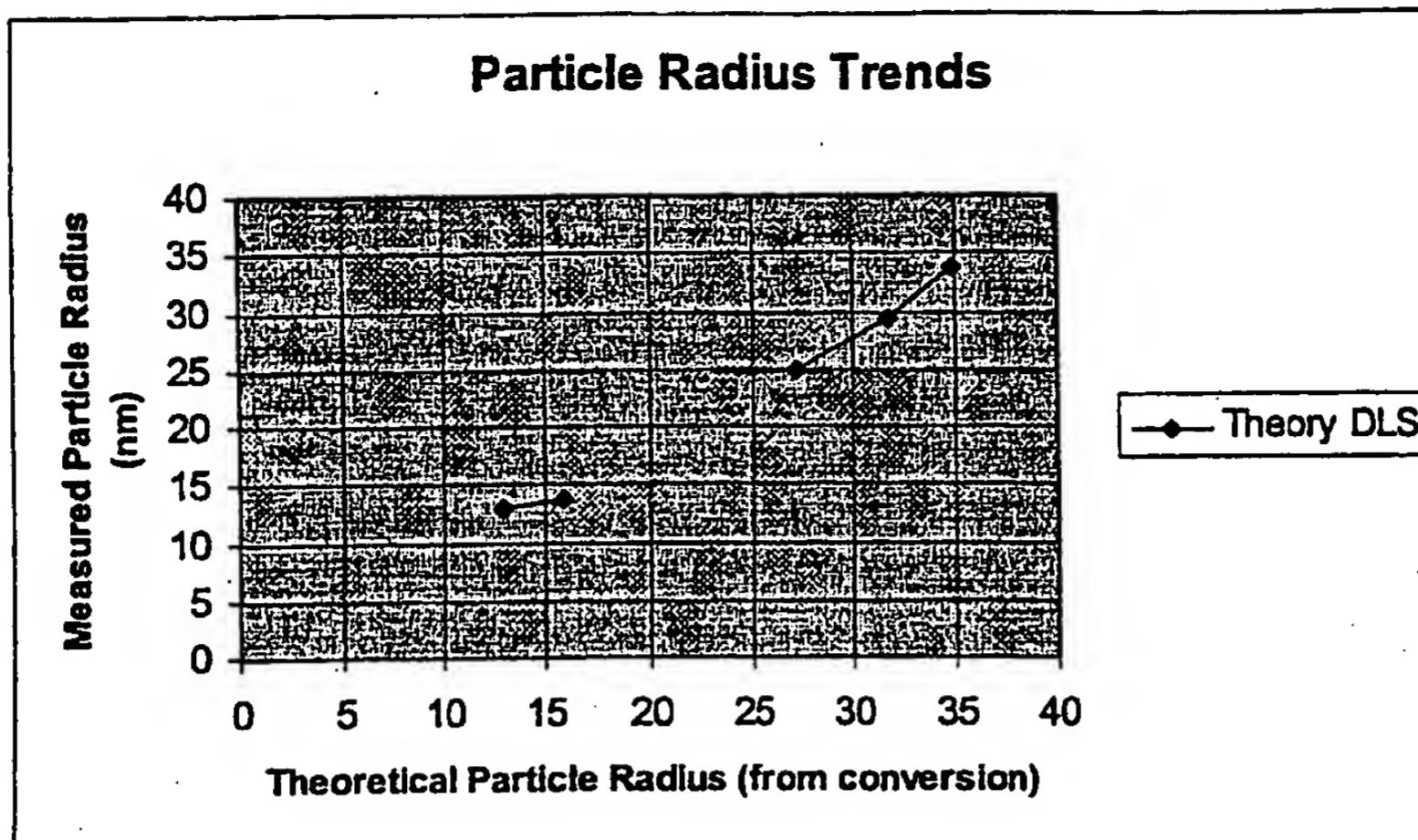


Fig. 14C

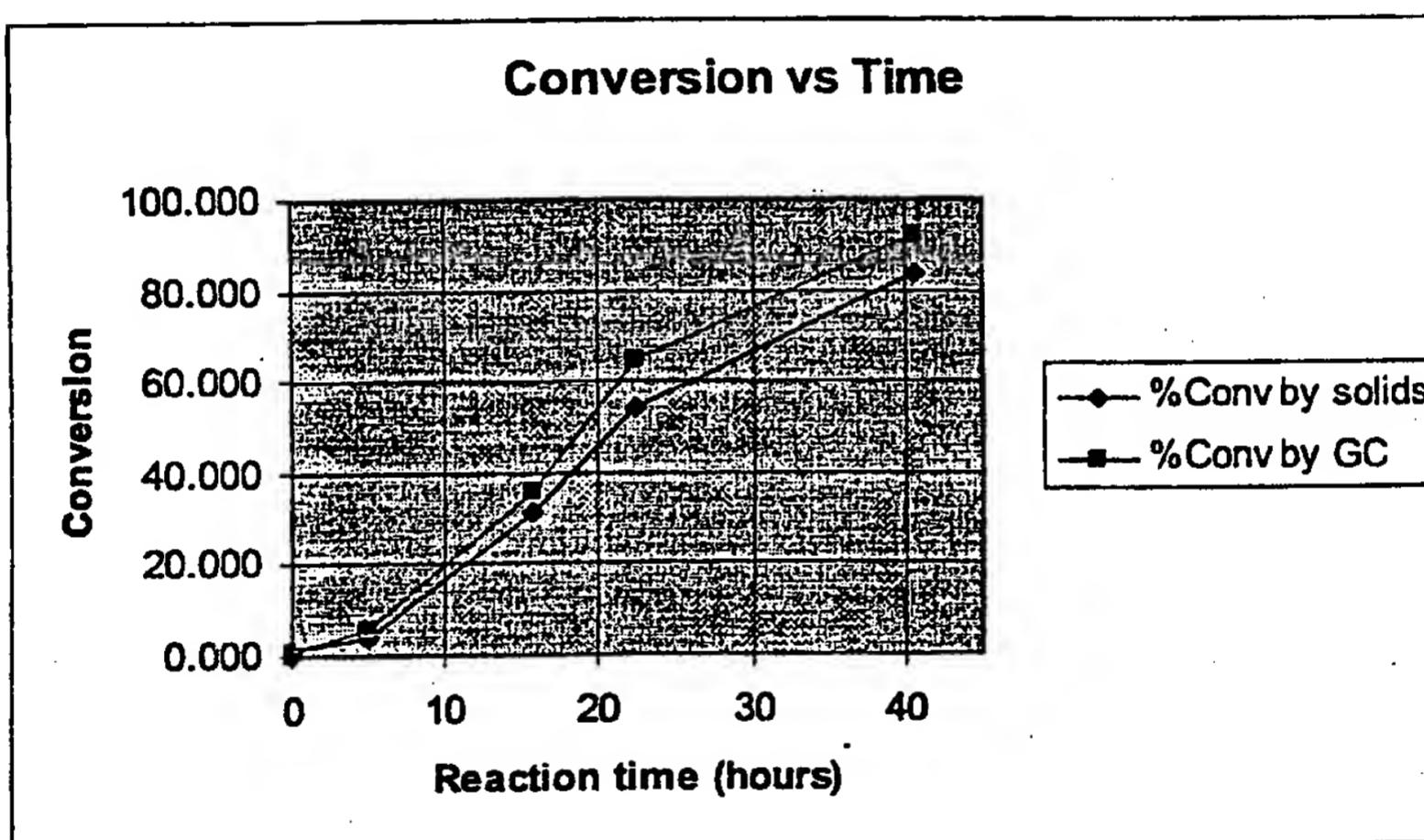


Fig. 14D

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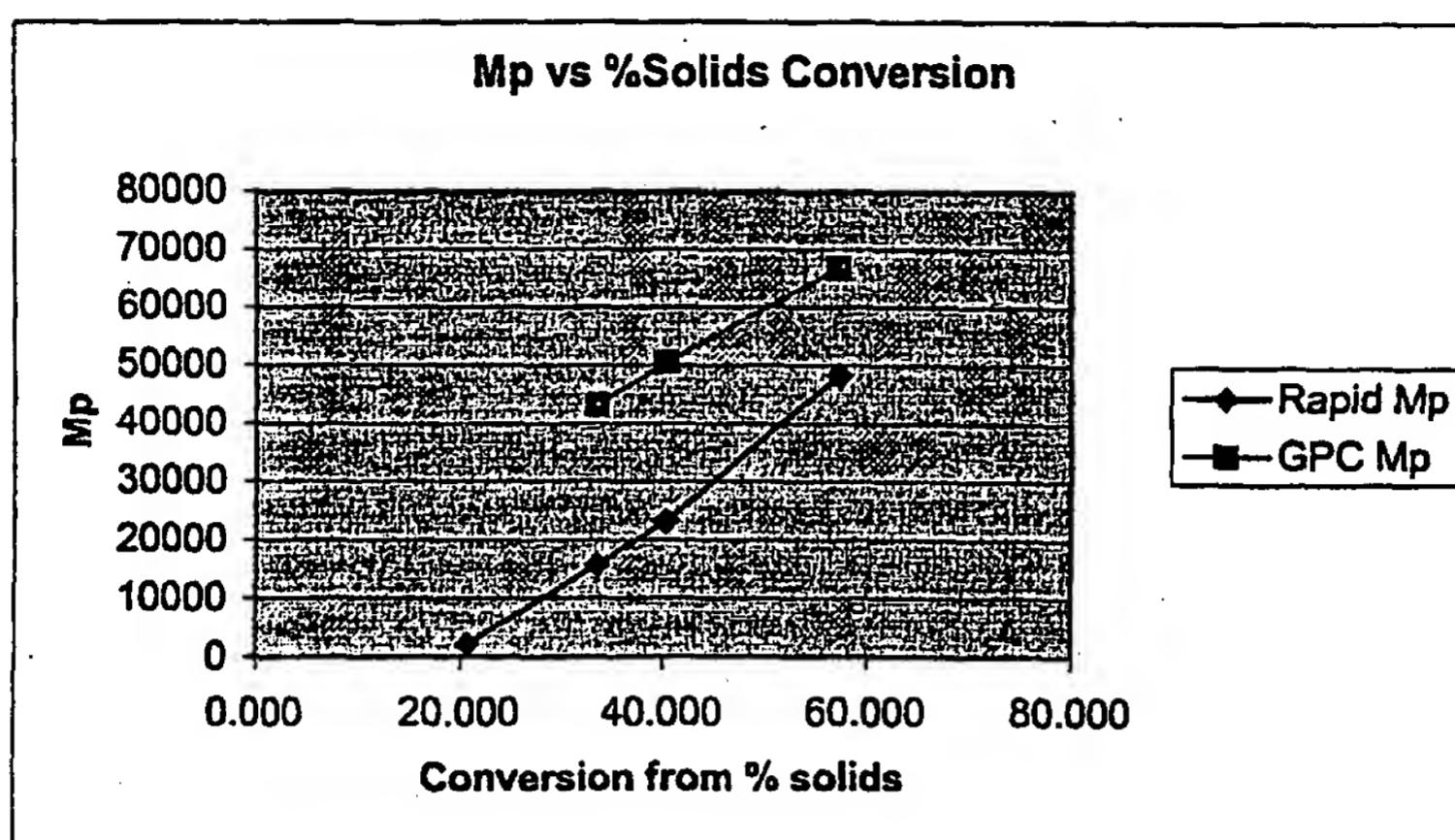


Fig. 15A

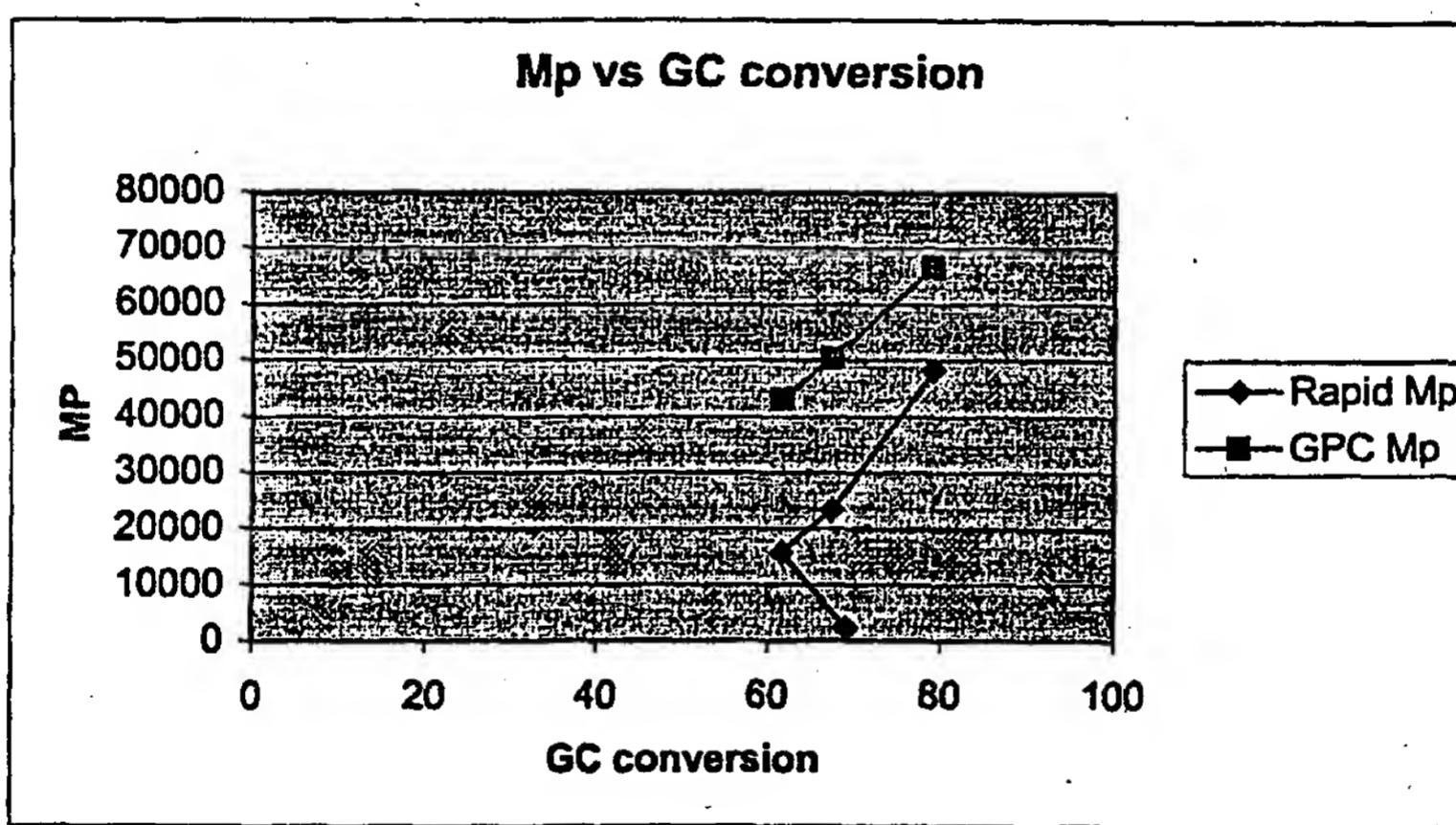


Fig 15B

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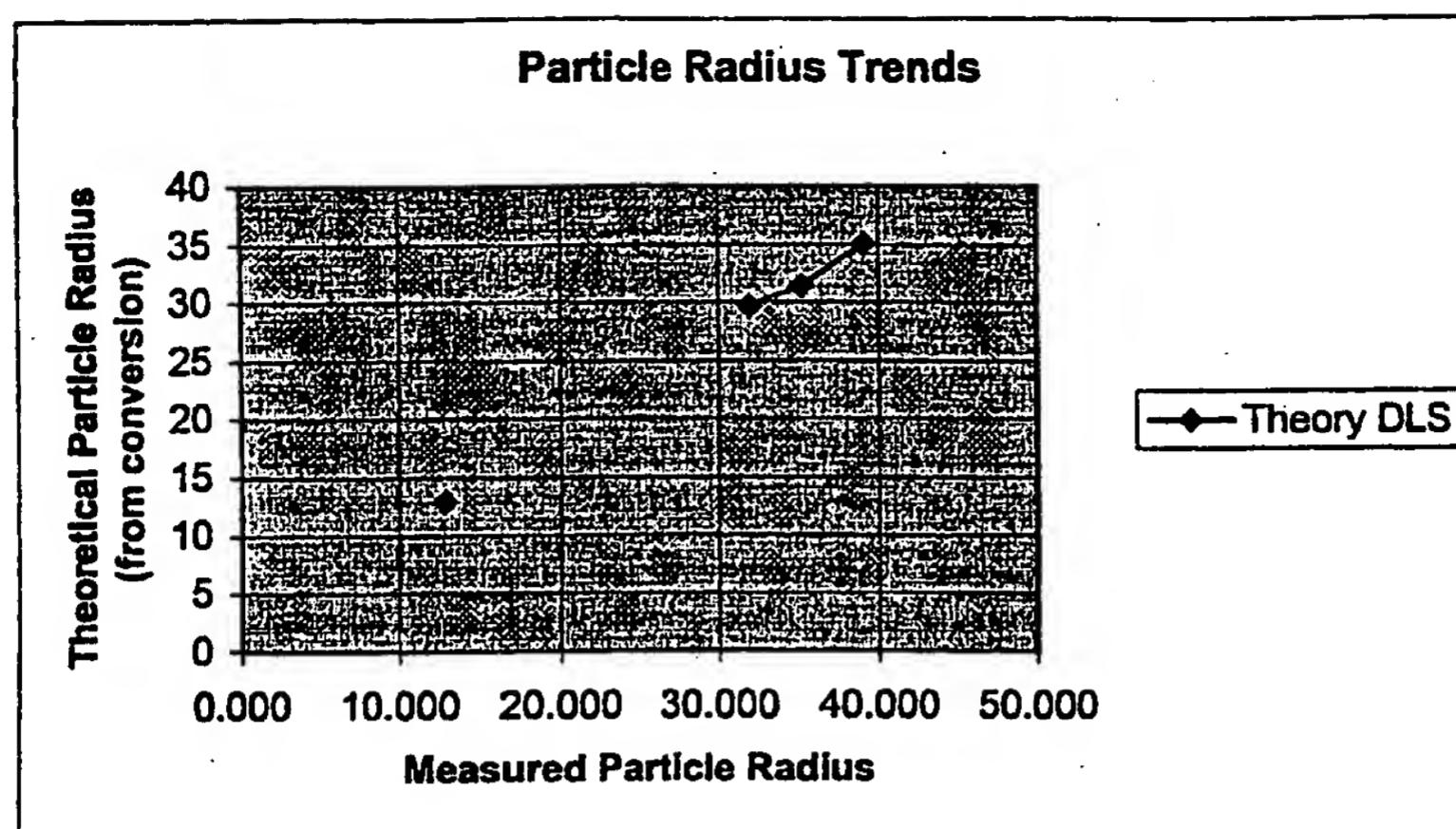


Fig 15C

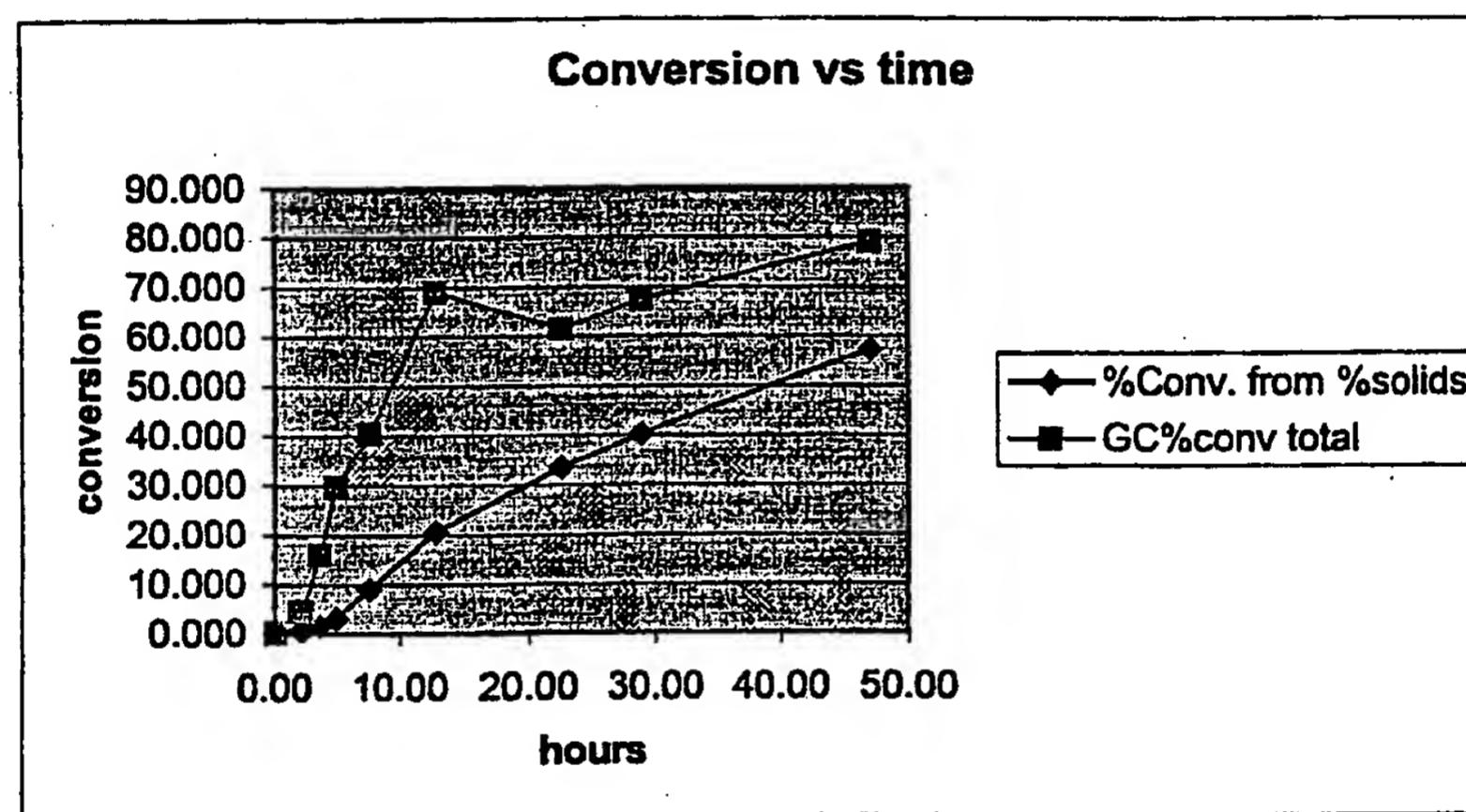


Fig 15D

## INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/US 00/06176

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F2/22 C08F2/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE COMPENDEX 'Online! ENGINEERING INFORMATION, INC., NEW YORK, NY, US MARESTIN CATHERINE ET AL: "Nitroxide mediated living radical polymerization of styrene in emulsion" Database accession no. EIX98364288894 XP002140836 abstract &amp; MACROMOLECULES; MACROMOLECULES JUN 16 1998 ACS, WASHINGTON, DC, USA, vol. 31, no. 12, 16 June 1998 (1998-06-16), pages 4041-4044,</p> <p style="text-align: center;">—/—</p>	1-77



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

Date of mailing of the international search report

22 June 2000

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Authorized officer

Pollio, M

**INTERNATIONAL SEARCH REPORT**

Information on patent family members.

International Application No

PCT/US 00/06176

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